

# PyIRoGlass: An Open-Source, Bayesian MCMC Algorithm for Fitting Baselines to FTIR Spectra of Basaltic-Andesitic Glasses

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The Python package can be accessed on GitHub at [github.com/sarahshi/PyIRoGlass](https://github.com/sarahshi/PyIRoGlass), and downloaded with PyPi. An implementation can be found on Google Colab at [colab.research.google.com/github/SarahShi/PyIRoGlass/blob/main/PyIRoGlass\\_RUN\\_colab.ipynb](https://colab.research.google.com/github/SarahShi/PyIRoGlass/blob/main/PyIRoGlass_RUN_colab.ipynb). If you encounter any issues, please reach out or raise an issue on GitHub. We welcome constructive feedback.

# PyIRoGlass: An Open-Source, Bayesian MCMC Algorithm for Fitting Baselines to FTIR Spectra of Basaltic-Andesitic Glasses

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## ABSTRACT

Quantifying volatile concentrations in magmas is critical for understanding magma storage, phase equilibria, and eruption processes. We present PyIRoGlass, an open-source Python package for quantifying concentrations of H<sub>2</sub>O and CO<sub>2</sub> species in the transmission FTIR spectra of basaltic to andesitic glasses. We leverage a dataset of natural melt inclusions and back-arc basin basalts with volatiles below detection to delineate the fundamental shape and variability of the baseline underlying the CO<sub>3</sub><sup>2-</sup> and H<sub>2</sub>O<sub>m,1635</sub> peaks, in the mid-infrared region. All Beer-Lambert Law parameters are examined to quantify associated uncertainties. PyIRoGlass employs Bayesian inference and Markov Chain Monte Carlo sampling to fit all probable baselines and peaks, solving for best-fit parameters and capturing covariance to offer robust uncertainty estimates. Results from PyIRoGlass agree with independent analyses of experimental devolatilized glasses (within 6%) and interlaboratory standards (10% for H<sub>2</sub>O, 6% for CO<sub>2</sub>). We determine new molar absorptivities for basalts,  $\epsilon_{\text{H}_2\text{O}_{t,3550}} = 63.03 \pm 4.47$  L/mol-cm and  $\epsilon_{\text{CO}_3^{2-}} = 303.44 \pm 9.20$  L/mol-cm; we additionally update the composition-dependent parameterizations of molar absorptivities, with their uncertainties, for all H<sub>2</sub>O and CO<sub>2</sub> species peaks. The open-source nature of PyIRoGlass ensures its adaptability and evolution as more data become available.

KEYWORDS: Volatiles; Ftir; Open-source; Python; Bayesian; Markov chain monte carlo.

## 1 INTRODUCTION

The loss of volatiles from magma during exsolution and degassing modulates phase equilibria [Sisson and Grove 1993], crystallinity [Blundy and Cashman 2001], density [Ochs III and Lange 1999], and viscosity [Hess and Dingwell 1996] from magma genesis to eruption. Major volatile components are H<sub>2</sub>O and CO<sub>2</sub>, both of which have strong pressure-dependent solubilities. Analyses of H<sub>2</sub>O and CO<sub>2</sub> in mineral-hosted melt inclusions are often utilized to estimate the conditions of magma storage and evolution, whereas analyses of synthetic glasses inform understandings of solubility and phase equilibria. H<sub>2</sub>O and CO<sub>2</sub> in volcanic glasses and synthetic products are commonly measured with two analytical techniques: Fourier Transform Infrared Spectroscopy (FTIR) and Secondary Ion Mass Spectrometry (SIMS). Here we focus on the FTIR spectroscopic technique, with the goal of improving the fitting of baselines and peaks in spectra and quantifying uncertainties in the resulting concentrations.

FTIR spectroscopy utilizes infrared light to excite materials, where infrared absorbance relates to the rotational, vibrational, and electronic energies of molecular bonds. Absorbance is proportional to concentration, allowing for the quantification of species with the Beer-Lambert Law:

$$c = \frac{AM}{\epsilon l \rho}, \quad (1)$$

where  $c$  is concentration,  $A$  is absorbance,  $M$  is the molar mass of the absorbing volatile species (g·mol<sup>-1</sup>),  $\epsilon$  is the absorptivity of the species (L·mol<sup>-1</sup>·m),  $l$  is the optical path

length or thickness (m), and  $\rho$  is density (kg·m<sup>-3</sup>). H<sub>2</sub>O and CO<sub>2</sub> species in silicate glasses absorb light in the near-infrared (12800-4000 cm<sup>-1</sup>) and mid-infrared (4000-200 cm<sup>-1</sup>) wavenumber regions (Figure 1). Volatile species vibration is observed through infrared absorbance, with the vibrations occurring as bending or stretching.

Dissolution of H<sub>2</sub>O in silicate liquids forms both molecular water (H<sub>2</sub>O<sub>m</sub>) and hydroxyl (OH<sup>-</sup>) species with concentration dependence. The vibration of H<sub>2</sub>O species combines bending and stretching energies in two dimensions [von Aulock et al. 2014]. Two H<sub>2</sub>O<sub>m</sub> peaks are found at ~5200 and ~1635 cm<sup>-1</sup>, and one OH<sup>-</sup> peak is found at ~4500 cm<sup>-1</sup> (Figure 1). Total H<sub>2</sub>O (H<sub>2</sub>O<sub>t</sub>=H<sub>2</sub>O<sub>m</sub>+OH<sup>-</sup>) is represented by the ~3550 cm<sup>-1</sup> peak. Linear relationships between absorbance and concentration dominate, but non-linear relationships can be introduced when increased sample thicknesses result in insufficient light transmission to the detector, causing the H<sub>2</sub>O<sub>t,3550</sub> peak to saturate with ragged peak tops and absorbances exceeding 2 [von Aulock et al. 2014; McIntosh et al. 2017]. When the H<sub>2</sub>O<sub>t,3550</sub> peak is saturated, the combination of H<sub>2</sub>O<sub>m,5200</sub> or H<sub>2</sub>O<sub>m,1635</sub> with OH<sub>4500</sub><sup>-</sup> species must be used instead. Dissolution of CO<sub>2</sub> forms molecular carbon dioxide (CO<sub>2</sub>) and carbonate (CO<sub>3</sub><sup>2-</sup>). The vibration of CO<sub>2</sub> species combines bending and stretching in three dimensions [von Aulock et al. 2014]. The CO<sub>2</sub> peak occurs at ~2350 cm<sup>-1</sup> and the CO<sub>3</sub><sup>2-</sup> doublet occurs at ~1515 and ~1430 cm<sup>-1</sup> (Figure 1). We restrict our treatment to basaltic to andesitic glasses, where the CO<sub>3</sub><sup>2-</sup> species dominate [Dixon and Pan 1995; Brooker et al. 2001a; b; Lowenstern 2001].

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The determination of volatile concentrations in silicate glasses requires the measurement of peak amplitudes or areas, defined as the difference in absorbance or integrated absorbance between peak and baseline. Variability and sub-  
 60 jectivity in baseline definition constitutes a significant, and typically unreported, uncertainty in most studies determining volatile concentrations. The  $\text{H}_2\text{O}_{\text{m},5200}$ ,  $\text{OH}_{4500}^-$ , and  $\text{H}_2\text{O}_{\text{t},3550}$  peaks in the near-infrared to mid-infrared region can be well quantified with linear to near-linear baselines be-  
 65 tween the two absorbance minima on either side of the peak. The  $\text{H}_2\text{O}_{\text{m},1635}$  peak and  $\text{CO}_3^{2-}$  doublet peaks pose greater challenges due to the steep and sharp increase of baseline absorbance at wavenumbers lower than  $1430\text{ cm}^{-1}$ . The convolution of the  $\text{H}_2\text{O}_{\text{m},1635}$  peak and the  $\text{CO}_3^{2-}$  doublet peak in glass spectra is a further complication. Devolatilized  
 70 glass baselines are the gold standard but are not possible to apply in melt inclusion studies, where large pieces of glass are not readily available. These devolatilized glasses are either synthesized from chemistry-matched glass powders or allowed to experimentally lose  $\text{H}_2\text{O}$  and  $\text{CO}_2$ . Previous studies have approximated baselines beneath the  $\text{H}_2\text{O}_{\text{m},1635}$  peak and the  $\text{CO}_3^{2-}$  doublet peaks using the spectra of chemistry-  
 75 and matrix-matched devolatilized glasses [e.g. Dixon et al. [1988] and Newman et al. [2000]], splines and flexicrves [e.g. Dixon and Stolper [1995]], linear functions [e.g. Behrens et al. [2009] and Shishkina et al. [2010, 2014]], and other curve functions [e.g. Dixon and Clague [2001]]. Such approaches are highly subjective, difficult to reproduce, and seldom reported with uncertainties. The main motivation in our development  
 85 of PyIRoGlass is to provide an open-source code that reproducibly fits transmission FTIR baselines and peaks with quantified uncertainties.

## 2 COMPONENTS OF PYIROGLASS

We examine each free parameter within the Beer-Lambert  
 90 Law ( $A$ ,  $\epsilon$ ,  $l$ ,  $\rho$ ) to develop PyIRoGlass, a Python implementation of a Bayesian algorithm with Markov Chain Monte Carlo (MCMC) sampling for fitting baselines and peaks for all  $\text{H}_2\text{O}$  and  $\text{CO}_2$  species in basaltic to andesitic glasses. There are several components to PyIRoGlass:

- I. **Section 2.1 Absorbance ( $A$ ):** We assess the fundamental shape and variability of the infrared baseline using principal component analysis (PCA) applied to a dataset of absorbance spectra for melt inclusions from the Aleutian arc [Rasmussen 2019] and back-arc basin glasses [Pearce et al. 1994] with volatiles below detection, relevant for basaltic to andesitic silicate melts. Application of PCA to this dataset of spectra with volatiles below detection allows for the assessment of the fundamental shape of the baseline and the spectral features contributing to its variability [Carvajal et al. 2016].
- II. **Section 2.2 Molar Absorptivity ( $\epsilon$ ):** We refit the relationships between molar absorptivity and composition with implicit iterative inversions, updating the parameterizations of Mandeville et al. [2002] and Dixon and Pan [1995] with new data, to derive molar absorptivity with uncertainty. We also calibrate new linear and

integrated molar absorptivities for a series of synthetic basalts [Moussallam et al. 2024].

- III. **Section 2.3 Thickness ( $l$ ), Density ( $\rho$ ):** To calculate thickness, we develop an automated implementation of the reflectance FTIR interference fringe method [Nishikida et al. 1996; Tamic et al. 2001; Wysoczanski and Tani 2006; Sun et al. 2007]. Because glass density is significantly affected by  $\text{H}_2\text{O}$  concentration, we outline an iterative approach to calculating density and  $\text{H}_2\text{O}$  concentration together.
- IV. **Section 2.4 PyIRoGlass integrates all the above steps** by employing a Bayesian algorithm with Markov Chain Monte Carlo sampling to find best-fit spectral baselines and peaks, given inputs of the infrared spectrum, thickness, and composition (to calculate molar absorptivity). The output of PyIRoGlass consists of peak amplitudes and concentrations calculated from the Beer-Lambert Law (Equation 1) for each  $\text{CO}_2$  and  $\text{H}_2\text{O}$  species peak, with their uncertainties.

### 2.1 Assessing Variability in Baselines and Peaks

We consider two different approaches to estimating baselines and extracting peak amplitudes. Baselines for the  $\text{H}_2\text{O}_{\text{m},5200}$ ,  $\text{OH}_{4500}^-$ , and  $\text{H}_2\text{O}_{\text{t},3550}$  peaks are nominally linear (Figure 1), so we use an asymmetric least squares method to determine the baseline, further discussed in Section 2.1.1. In the wavenumber region between  $2400$  and  $1250\text{ cm}^{-1}$ , the baseline has a complex shape beneath the  $\text{H}_2\text{O}_{\text{m},1635}$  peak and the  $\text{CO}_3^{2-}$  and  $\text{CO}_2^{1430}$  doublet peaks. Moreover, the tail on the  $\text{H}_2\text{O}_{\text{m},1635}$  peak can convolute with the  $\text{CO}_3^{2-}$  peak. We thus develop an empirical model for the baseline and peaks in this region, based on a dataset of natural glasses with volatiles below detection, described in Section 2.1.2.

#### 2.1.1 Asymmetric Least Squares Baselines for $\text{H}_2\text{O}_{\text{m},5200}$ , $\text{OH}_{4500}^-$ and $\text{H}_2\text{O}_{\text{t},3550}$ Peaks

The  $\text{H}_2\text{O}_{\text{m},5200}$ ,  $\text{OH}_{4500}^-$ , and  $\text{H}_2\text{O}_{\text{t},3550}$  baselines are fit with the asymmetric least squares (ALS) method [Eilers 2004]. ALS is commonly used as an iterative solver for processing Raman and infrared spectra with interpolated baseline fittings, balancing smoothness and asymmetry while remaining fast [Eilers 2004; Peng et al. 2010; Lee et al. 2017]. Data are pre-processed by first applying a median filter to remove single spike noise. We vary the peak fitting region surrounding each peak and fit three repeat baselines with ALS to assess uncertainty within the peak shape and location. Nominal peak fitting regions are varied by  $\pm 200\text{ cm}^{-1}$  for the  $\text{H}_2\text{O}_{\text{t},3550}$  peak and  $\pm 25\text{ cm}^{-1}$  for the  $\text{H}_2\text{O}_{\text{m},5200}$  and  $\text{OH}_{4500}^-$  peaks to fit the range of potential peaks and to assess the uncertainty in peak fitting region. The baselines are subtracted from the peak. The three baseline-subtracted peaks are processed with kriging interpolation to reduce noise and to obtain maximum peak amplitude [Krige 1951]. Kriging interpolation utilizes sample data of limited resolution to predict and interpolate data of higher resolution with estimates of uncertainty in each interpolated value. The mean peak absorbance and standard deviation in absorbance are determined from

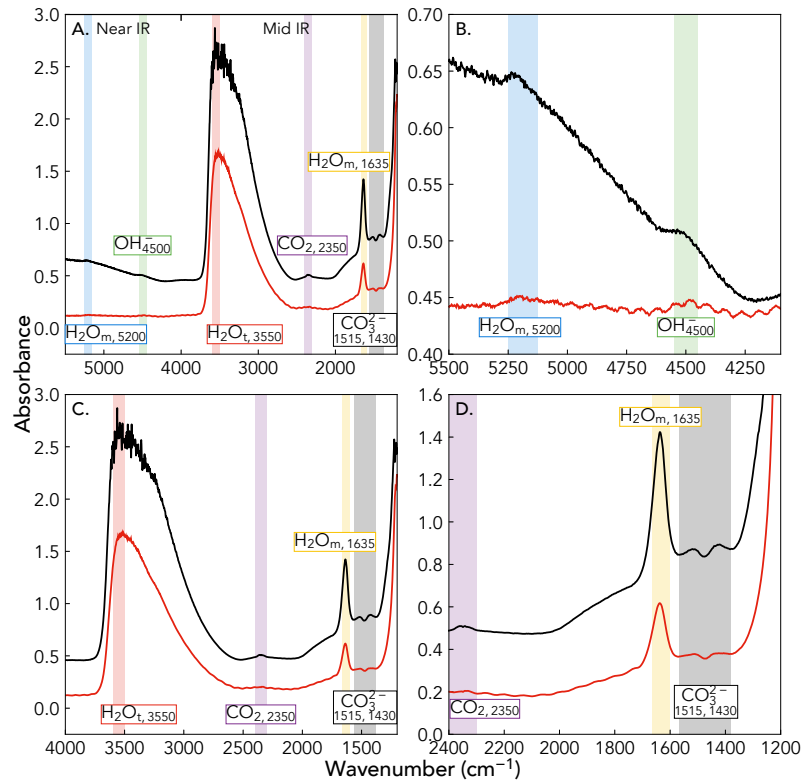


Figure 1: Transmission FTIR spectra of olivine-hosted melt inclusions VF18-AC4-OL49 (black) and VF18-AC4-OL53 (red), from Volcán de Fuego, Guatemala (see Section 3.2). OL49 is  $91 \pm 3 \mu\text{m}$  thick and OL53 is  $39 \pm 3 \mu\text{m}$  thick. Greater thicknesses increase absorbance and contribute to saturation, seen when the absorbance of  $\text{H}_2\text{O}_{\text{t},3550}$  exceeds 2 and the peak is ragged. A. Transmission FTIR spectra through the near-IR and mid-IR regions. B.  $\text{H}_2\text{O}_{\text{m},5200}$  and  $\text{OH}_{4500}^-$  peaks in the near-IR region. OL53's absorbance spectrum is shifted upwards for visualization. OL49 has strong signal-to-noise ratios with well-defined peaks, but OL53 has low signal-to-noise ratios with interference fringes. Saturated samples have high signal-to-noise ratio peaks in the near-IR region. OL49 contains  $1.82 \pm 0.35 \text{ wt.} \% \text{H}_2\text{O}_{\text{m},5200}$  and  $1.25 \pm 0.26 \text{ wt.} \% \text{OH}_{4500}^-$ . OL53's near-IR peaks are not considered given lack of saturation in  $\text{H}_2\text{O}_{\text{t},3550}$ . C.  $\text{H}_2\text{O}_{\text{t},3550}$  peak. OL49 is saturated in  $\text{H}_2\text{O}_{\text{t},3550}$ , introducing non-linearity into the Beer-Lambert Law and preventing usage. OL53 contains  $4.04 \pm 0.43 \text{ wt.} \% \text{H}_2\text{O}_{\text{t},3550}$ . D.  $\text{H}_2\text{O}_{\text{m},1635}$  peak and  $\text{CO}_3^{2-}$  doublet. Rapid absorbance upturn following the  $\text{CO}_3^{2-}$  peak prevents a linear baseline from being fitted, motivating the development of PylRoGlass. OL49 contains  $1.30 \pm 0.19 \text{ wt.} \% \text{H}_2\text{O}_{\text{m},1635}$  and  $753 \pm 36 \text{ ppm CO}_2$  and OL53 contains  $1.49 \pm 0.26 \text{ wt.} \% \text{H}_2\text{O}_{\text{m},1635}$  and  $735 \pm 62 \text{ ppm CO}_2$ , with concentrations from PylRoGlass.

the three baseline-subtracted peaks.  $\text{H}_2\text{O}_{\text{t},3550}$  saturation, observed when the maximum absorbance of  $\text{H}_2\text{O}_{\text{t},3550}$  exceeds 2, prompts the return of an error message and suggests the use of the  $\text{H}_2\text{O}_{\text{m},1635}$  and  $\text{OH}_{4500}^-$  peaks for determining  $\text{H}_2\text{O}_{\text{t}}$ . The use of the  $\text{H}_2\text{O}_{\text{m},1635}$  over the  $\text{H}_2\text{O}_{\text{m},5200}$  peak is further discussed in Section 3.4.

### 2.1.2 Baselines for the $\text{H}_2\text{O}_{\text{m},1635}$ , $\text{CO}_3^{2-}$ and $\text{CO}_3^{2-}$ Peaks

The compositional variability and small size of melt inclusions (often  $< 50 \mu\text{m}$  in diameter) present challenges for determining FTIR baselines for the  $\text{H}_2\text{O}_{\text{m},1635}$  and  $\text{CO}_3^{2-}$  doublet. While the FTIR spectra of experimentally devolatilized glasses are one of the best ways to determine baselines for the complex spectral region underlying the peaks, these glasses unfortunately do not exist for all melt inclusion compositions. The approach we have taken is to use natural melt inclusions and back-arc basin (BAB) glasses, with volatiles below detection, to determine a family of baseline shapes in this spec-

tral region. Melt inclusions with volatiles below detection are typically considered failures in the attempt to characterize the volatile concentrations of magmas, reflecting potential decrepitation [Maclennan 2017], high detection limits (Section 3.6), or simply volatile-poor systems. We make use of a dataset of glasses with volatiles below detection here to define baseline shapes for natural basalts and andesites, with raw spectra shown in Figure 2. The dataset consists of 57 transmission FTIR spectra of Aleutian melt inclusions [Rasmussen 2019] and back-arc basin glasses [Newman et al. 2000] that span a compositional range from basalt to andesite ( $\text{SiO}_2 = 43\text{-}60 \text{ wt.} \%$ ,  $\text{TiO}_2 = 0.7\text{-}5.4 \text{ wt.} \%$ ,  $\text{Al}_2\text{O}_3 = 10.9\text{-}20.8 \text{ wt.} \%$ ,  $\text{FeO} = 6.3\text{-}22.2 \text{ wt.} \%$ ,  $\text{MgO} = 2.1\text{-}7.0 \text{ wt.} \%$ ,  $\text{CaO} = 4.3\text{-}15.6 \text{ wt.} \%$ ,  $\text{Na}_2\text{O} = 2.2\text{-}4.4 \text{ wt.} \%$ ,  $\text{K}_2\text{O} = 0.2\text{-}1.9 \text{ wt.} \%$ ). Some spectra lack both detectable  $\text{H}_2\text{O}_{\text{m},1635}$  and  $\text{CO}_3^{2-}$  peaks ( $n = 14$ ), while others have  $\text{H}_2\text{O}_{\text{m},1635}$  peaks with no detectable  $\text{CO}_3^{2-}$  peaks ( $n = 43$ ).

Definition of baseline and peak shapes is iterative. First, we use the absorbance spectra, with both  $\text{H}_2\text{O}_{\text{m},1635}$  and



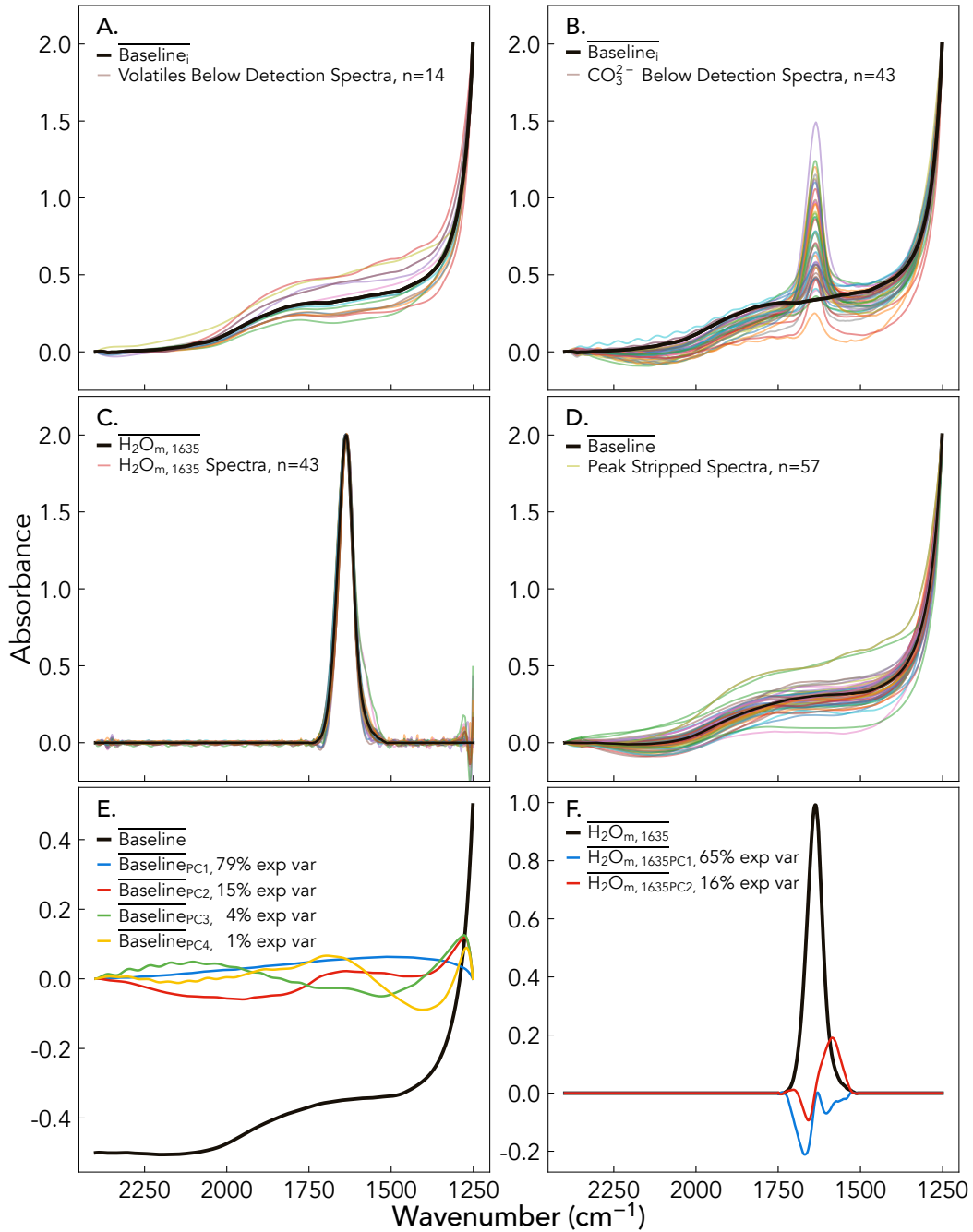


Figure 2: Transmission FTIR spectra for the dataset of basaltic to andesitic melt inclusions and glasses with volatiles below detection used to identify the range of possible baselines for fitting  $\text{H}_2\text{O}_{\text{m},1635}$  and  $\text{CO}_3^{2-}$  doublet peaks. Spectra range from 16-136  $\mu\text{m}$  and have 1  $\mu\text{m}$  normalized peak amplitudes of less than  $10^{-4}$ . A. Absorbance spectra in the natural dataset used to generate the initial mean baseline ( $\text{Baseline}_i$ ). Spectra are linearly rescaled to span an absorbance range of 0-2 in the wavenumber fitting range of 2400 to 1250  $\text{cm}^{-1}$ . B. Absorbance spectra with  $\text{CO}_3^{2-}$  below detection are fit with  $\text{Baseline}_i$  in a least squares optimization to identify the  $\text{H}_2\text{O}_{\text{m},1635}$  peak shape, allowing for peak-stripping to generate synthetic spectra with volatiles below detection. These spectra are similarly linearly rescaled. C.  $\text{H}_2\text{O}_{\text{m},1635}$  peaks identified by least squares baseline subtraction are used to generate the mean  $\text{H}_2\text{O}_{\text{m},1635}$  peak shape ( $\text{H}_2\text{O}_{\text{m},1635}$ ) and two associated principal components of  $\text{H}_2\text{O}_{\text{m},1635\text{PC}1-2}$ . D. The full dataset of spectra with volatiles below detection following peak-stripping of absorbance spectra, using least squares fitting of  $\text{H}_2\text{O}_{\text{m},1635}$  and  $\text{H}_2\text{O}_{\text{m},1635\text{PC}1-2}$ . These spectra generate the final mean baseline ( $\text{Baseline}$ ) and four associated principal components of  $\text{Baseline}_{\text{PC}1-4}$  shown in panel E. E.  $\text{Baseline}$  and  $\text{Baseline}_{\text{PC}1-4}$  describing variability in the baseline. Panel text shows the percentage of explained variance by that principal component (exp var). F.  $\text{H}_2\text{O}_{\text{m},1635}$  and  $\text{H}_2\text{O}_{\text{m},1635\text{PC}1-2}$  describing variability in the peak.

205  $\text{CO}_3^{2-}$  below detection, to generate an initial mean baseline or Baseline<sub>i</sub>; (Figure 2A). Spectra are shifted and scaled to ensure equal absorbance in the wavenumber fitting range from 2400 to 1250  $\text{cm}^{-1}$ . We describe variability within the baseline with principal component analysis (PCA). Four principal components (PC) describe more than 95% of the variance within the initial baseline. These spectra are confirmed to have  $\text{H}_2\text{O}_{\text{m},1635}$  or  $\text{CO}_3^{2-}$  below detection, as the 1  $\mu\text{m}$  normalized peak amplitudes are less than  $10^{-4}$  across thicknesses of 16-136  $\mu\text{m}$  with an initial least squares baseline fitting with Baseline<sub>i</sub>. The 1  $\mu\text{m}$  normalized peak amplitudes of  $10^{-4}$  establishes an initial operational limit for recognizable peaks, but the detection limits will be quantified later in Section 3.6.

Next, we use the spectra containing  $\text{H}_2\text{O}_{\text{m},1635}$  but with  $\text{CO}_3^{2-}$  below detection to define peak shapes and to create a greater number of baselines. Spectra with  $\text{H}_2\text{O}_{\text{m},1635}$  but with  $\text{CO}_3^{2-}$  below detection are first fit for the  $\text{H}_2\text{O}_{\text{m},1635}$  peak, then stripped of it (Figure 2B). We fit the spectra with Baseline<sub>i</sub> and four principal components to isolate the shape of the  $\text{H}_2\text{O}_{\text{m},1635}$  peak, which is neither Gaussian nor Lorentzian, due to the rapid downturn of the  $\text{H}_2\text{O}_{\text{m},1635}$  peak. We thus identify the mean  $\text{H}_2\text{O}_{\text{m},1635}$  peak ( $\overline{\text{H}_2\text{O}_{\text{m},1635}}$ ) and describe variability within the peak with PCA (Figure 2C, Figure 2F). The first two principal components of  $\overline{\text{H}_2\text{O}_{\text{m},1635\text{PC}_{1-2}}}$  accommodate variations in  $\text{H}_2\text{O}_{\text{m},1635}$  peak shape and location from its nominal peak location of  $\sim 1635$   $\text{cm}^{-1}$ .  $\overline{\text{H}_2\text{O}_{\text{m},1635\text{PC}_1}}$  is similar to the negative second derivative of the  $\text{H}_2\text{O}_{\text{m},1635}$  peak;  $\overline{\text{H}_2\text{O}_{\text{m},1635\text{PC}_2}}$  is similar to the first derivative of the  $\text{H}_2\text{O}_{\text{m},1635}$  peak. We restrict our analysis to the first two principal components, which account for over 80% of the variance within the peak shape. Subsequent principal components introduce considerable noise and were therefore excluded. Identification of the  $\text{H}_2\text{O}_{\text{m},1635}$  peak shape further allows for  $\text{H}_2\text{O}_{\text{m},1635}$  peak subtraction from the spectra with  $\text{CO}_3^{2-}$  below detection with least squares, generating additional spectra with  $\text{H}_2\text{O}_{\text{m},1635}$  and  $\text{CO}_3^{2-}$  below detection. Spectra with  $\text{CO}_3^{2-}$  below detection are thus converted to spectra with both  $\text{H}_2\text{O}_{\text{m},1635}$  and  $\text{CO}_3^{2-}$  below detection (Figure 2D).

We iteratively identify and define the mean baseline (Baseline) with associated variability described by the addition or subtraction of four principal components of Baseline<sub>PC<sub>1-4</sub></sub> (Figure 2E, Figure 3). For samples that contain both  $\text{H}_2\text{O}_{\text{m},1635}$  and  $\text{CO}_3^{2-}$ , we disentangle the convoluted tails of the overlapping  $\text{H}_2\text{O}_{\text{m},1635}$  and the  $\text{CO}_{3,1515}^{2-}$  peaks by identifying  $\overline{\text{H}_2\text{O}_{\text{m},1635}}$  with  $\overline{\text{H}_2\text{O}_{\text{m},1635\text{PC}_{1-2}}}$  and the Gaussian  $\text{CO}_3^{2-}$  peaks (Figure 2F, Figure 4). Given the sharp upturn in absorbance while approaching 1250  $\text{cm}^{-1}$ , we provide additional accommodation for shifting and tilting the  $\text{H}_2\text{O}_{\text{m},1635}$  peak and  $\text{CO}_3^{2-}$  doublet with a linear shift. The code associated with baseline generation is available in the PjIRoGlass GitHub repository.

We can therefore describe the range of possible baselines while simultaneously fitting peaks appropriate for basaltic to andesitic glasses with the net equation:

$$\hat{A} = \hat{B} + \text{H}_2\text{O}_{\text{m},1635}^{\hat{}} + \text{CO}_3^{2-}^{\hat{}} + \hat{L}, \quad (2)$$

with  $\hat{A}$  as the best-fit absorbance spectrum.  $\hat{B}$ , the best-fit baseline, is fit by:

$$\hat{B} = x_0\bar{B} + x_1\bar{B}_{\text{PC}_1} + x_2\bar{B}_{\text{PC}_2} + x_3\bar{B}_{\text{PC}_3} + x_4\bar{B}_{\text{PC}_4}, \quad (3)$$

where the  $x_n$  terms are best-fit scaling coefficients,  $\bar{B}$  is the mean baseline, and  $\bar{B}_{\text{PC}_n}$  is the  $n$ -th principal component describing variability in the baseline.

$\text{H}_2\text{O}_{\text{m},1635}^{\hat{}}$ , the best-fit  $\text{H}_2\text{O}_{\text{m},1635}$  peak, is fit by:

$$\text{H}_2\text{O}_{\text{m},1635}^{\hat{}} = y_0\overline{\text{H}_2\text{O}_{\text{m},1635}} + y_1\overline{\text{H}_2\text{O}_{\text{m},1635\text{PC}_1}} + y_2\overline{\text{H}_2\text{O}_{\text{m},1635\text{PC}_2}}, \quad (4)$$

where the  $y_n$  terms are best-fit scaling coefficients,  $\overline{\text{H}_2\text{O}_{\text{m},1635}}$  is the mean  $\text{H}_2\text{O}_{\text{m},1635}$  peak, and  $\overline{\text{H}_2\text{O}_{\text{m},1635\text{PC}_n}}$  is the  $n$ -th principal component describing variability in the  $\text{H}_2\text{O}_{\text{m},1635}$  peak. The  $\overline{\text{H}_2\text{O}_{\text{m},1635}}$  term fits peak amplitude and the  $\overline{\text{H}_2\text{O}_{\text{m},1635\text{PC}_{1-2}}}$  terms accommodate lateral variations in peak location.

$\text{CO}_3^{2-}^{\hat{}}$ , the best-fit  $\text{CO}_3^{2-}$  peak, is fit by:

$$\text{CO}_3^{2-}^{\hat{}} = \frac{a}{2\sigma^2} \cdot e^{-(\nu^- - \mu)^2}, \quad (5)$$

where  $a$  is the peak amplitude,  $\sigma$  is the peak half-width,  $\nu^-$  is the wavenumber fitting range, and  $\mu$  is the central wavenumber of the peak. The  $\mu$  parameter allows for slight deviations ( $\pm 15$   $\text{cm}^{-1}$ ) in peak location.

$\hat{L}$ , the linear function allowing for tilt and vertical offset of the spectrum, is described by:

$$\hat{L} = m\nu^- + b, \quad (6)$$

where  $m$  is the slope,  $\nu^-$  is the wavenumber fitting range, and  $b$  is the intercept.

Peak and baseline coefficients and parameters are sampled and fit concurrently within an MCMC framework with Bayesian inference to accounts for uncertainties and covariance. The best-fit peak amplitudes and uncertainties for the  $\text{H}_2\text{O}_{\text{m},1635}$  and  $\text{CO}_3^{2-}$  doublet peaks are exported from the algorithm and used to determine volatile concentrations with uncertainties.

## 2.2 Calibrating Molar Absorptivity or Extinction Coefficient

Molar absorptivities or extinction coefficients ( $\epsilon$ ) determine the intensity at which light attenuates when passing through a material, relating absorbance to concentration. Calibration of  $\epsilon$  involves pairing measurements of transmission FTIR absorbance spectra with  $\text{H}_2\text{O}$  or  $\text{CO}_2$  concentrations determined by an independent volatile analytical technique.  $\epsilon$  is dependent on glass composition — the  $\epsilon$  related to  $\text{H}_2\text{O}$  species is dependent on the tetrahedral cation fraction of  $\tau = (\text{Si}^{4+} + \text{Al}^{3+})/\text{total cations}$ , while the  $\epsilon$  related to  $\text{CO}_2$  species is dependent on the cation fraction of  $\text{Na}^+ / (\text{Na}^+ + \text{Ca}^{2+})$ , which we will term  $\eta$ .  $\epsilon$  data are drawn

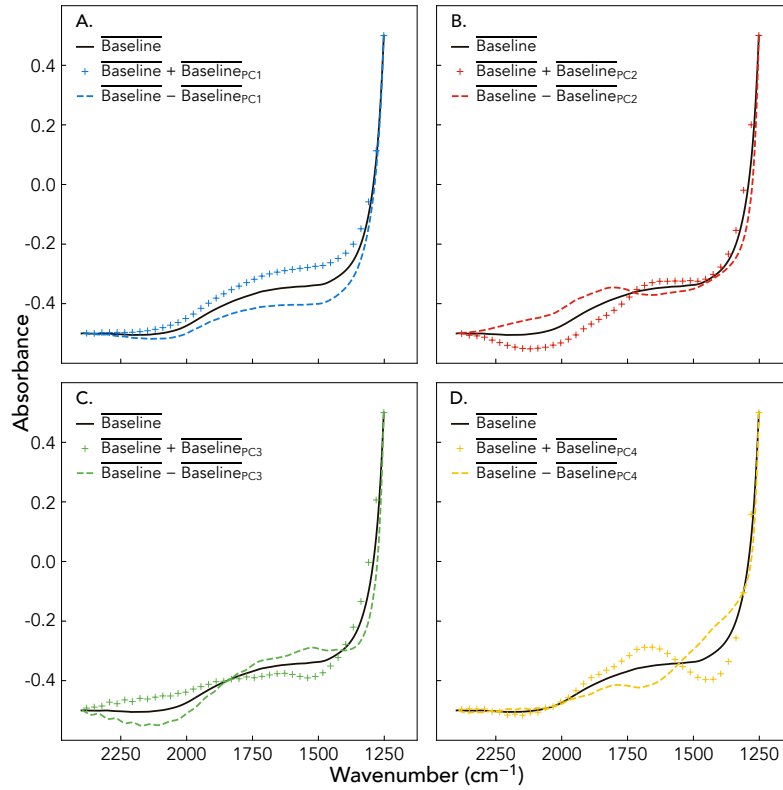


Figure 3: Mean baseline with volatiles below detection ( $\overline{\text{Baseline}}$ ) with  $\overline{\text{Baseline}}_{\text{PC1-4}}$  describing variability within the baseline. A.  $\overline{\text{Baseline}} \pm \overline{\text{Baseline}}_{\text{PC1}}$  most closely resembles the range of baselines in Figure 2D. B.  $\overline{\text{Baseline}} \pm \overline{\text{Baseline}}_{\text{PC2}}$ . C.  $\overline{\text{Baseline}} \pm \overline{\text{Baseline}}_{\text{PC3}}$ . D.  $\overline{\text{Baseline}} \pm \overline{\text{Baseline}}_{\text{PC4}}$ .

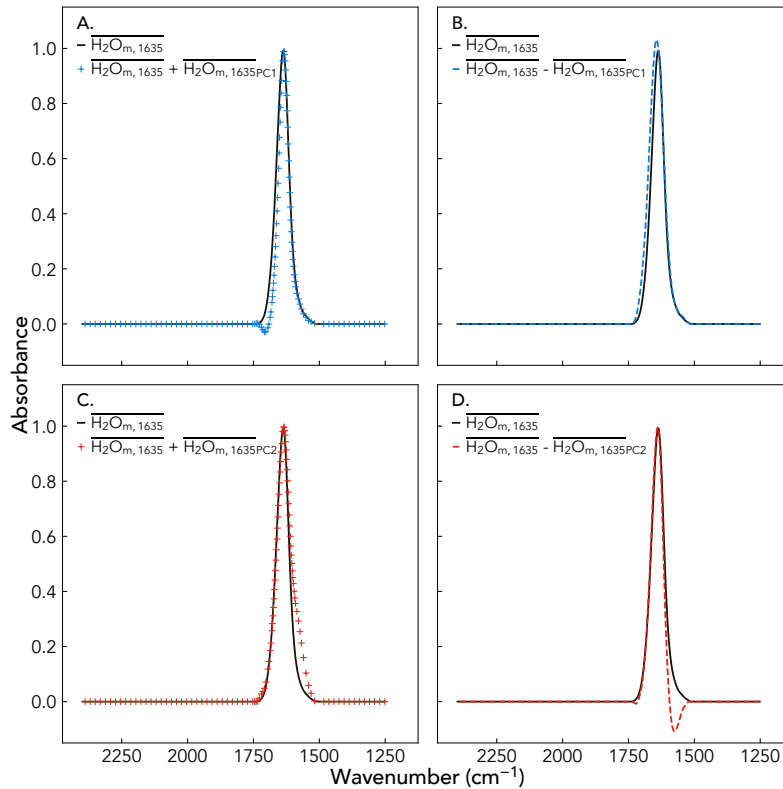


Figure 4: Mean  $\overline{\text{H}_2\text{O}_{m,1635}}$  peak ( $\overline{\text{H}_2\text{O}_{m,1635}}$ ) with  $\overline{\text{H}_2\text{O}_{m,1635}}_{\text{PC1-2}}$  describing variability in the nominal peak location. A.  $\overline{\text{H}_2\text{O}_{m,1635}} + \overline{\text{H}_2\text{O}_{m,1635}}_{\text{PC1}}$ . B.  $\overline{\text{H}_2\text{O}_{m,1635}} - \overline{\text{H}_2\text{O}_{m,1635}}_{\text{PC1}}$ . C.  $\overline{\text{H}_2\text{O}_{m,1635}} + \overline{\text{H}_2\text{O}_{m,1635}}_{\text{PC2}}$ . D.  $\overline{\text{H}_2\text{O}_{m,1635}} - \overline{\text{H}_2\text{O}_{m,1635}}_{\text{PC2}}$ .

from studies with independent methods of volatile measurement, such as Elemental Analyzer (EA), Elastic Recoil Detection Analysis (ERDA), experimental mass balance, Karl Fischer Titration (KFT), manometry, Nuclear Magnetic Resonance (NMR), Nuclear Reaction Analysis (NRA), Secondary Ion Mass Spectrometry (SIMS), and vacuum heating.

We calibrate linear molar absorptivities (peak amplitude-based,  $\epsilon$ ) and integrated molar absorptivities (peak area-based,  $\epsilon_i$ ) for the  $\text{H}_2\text{O}_{\text{t},3550}$  and  $\text{CO}_3^{2-}$  peaks of an array of synthetic basalts (Table 3) analyzed by ERDA and SIMS for  $\text{H}_2\text{O}$  and NRA for  $\text{CO}_2$  by Moussallam et al. [2024] (Supplement Section 2.1). We further compile a new dataset of published  $\epsilon$  from studies performed between 1982 to 2024 (Table 1). In the full dataset,  $\tau$  spans the range of 0.50-0.90 and  $\eta$  spans 0.23-0.84. We examine whether these compositional parameters remain the best descriptors of  $\epsilon$ . We refit the linear relationships between  $\epsilon_{\text{H}_2\text{O}_{\text{m},5200}}$ ,  $\epsilon_{\text{OH}^-_{4500}}$ ,  $\epsilon_{\text{H}_2\text{O}_{\text{t},3550}}$ ,  $\epsilon_{\text{H}_2\text{O}_{\text{m},1635}}$ , and  $\epsilon_{\text{CO}_3^{2-}}$  and their corresponding compositional parameters using a Newtonian inversion technique. This inclusion of more recent data and broader compositional ranges was done following the last parameterizations of  $\epsilon$  with  $\tau$  by Mandeville et al. [2002] and with  $\eta$  by Dixon and Pan [1995].

$\epsilon$  related to  $\text{H}_2\text{O}$  species increases with  $\tau$ , reflecting increased polymerization of the glass [Stolper 1982]. Tetrahedral cations have also been proposed to compete with non-tetrahedral cations ( $M = \text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Na}^+$ ) to bond with free hydroxyl groups in melt [Pandya et al. 1992; Mercier et al. 2010]. More depolymerized melts will have higher proportions of free hydroxyl, which translates to more  $M\text{-(OH)}_x$  bonding and hydrogen bonding [Xue 2009; Mercier et al. 2010]. Dixon et al. [1995] and Mandeville et al. [2002] demonstrate the dependence of the  $\epsilon_{\text{H}_2\text{O}_{\text{m},5200}}$ ,  $\epsilon_{\text{OH}^-_{4500}}$ , and  $\epsilon_{\text{H}_2\text{O}_{\text{m},1635}}$  on glass  $\tau$ .  $\epsilon_{\text{H}_2\text{O}_{\text{t},3550}}$  is also positively correlated with  $\tau$ , but this relationship is less straightforward than originally thought [Mercier et al. 2010]. Quench temperatures and rates drive the formation of variable proportions of  $\text{H}_2\text{O}_{\text{m}}$  and  $\text{OH}^-$  [Silver and Stolper 1989; Stolper 1989].  $\epsilon_{\text{H}_2\text{O}_{\text{t},3550}}$  is thus considered as a combination of two endmember molar absorptivities,  $\epsilon_{\text{H}_2\text{O}_{\text{m},3550}}$  and  $\epsilon_{\text{OH}^-_{3550}}$ , multiplied by the relative proportion of each respective species [Newman et al. 1986; Okumura et al. 2003; McIntosh et al. 2017]. Studies quantifying  $\epsilon_{\text{H}_2\text{O}_{\text{m},3550}}$  and  $\epsilon_{\text{OH}^-_{3550}}$  are the gold standard, but are currently limited in compositional range. McIntosh et al. [2017] considered the range of  $\tau = 0.746\text{-}0.800$ , spanning silicic compositions with rhyolitic to albitic glasses. More experiments are needed to properly quantify the species-dependent nature of the  $\text{H}_2\text{O}_{\text{t},3550}$  peak. We find a positive relationship between  $\epsilon_{\text{H}_2\text{O}_{\text{t},3550}}$  and  $\tau$ , despite complications presented by speciation. While endmember  $\epsilon$  data for the  $\text{H}_2\text{O}_{\text{t},3550}$  peak remain limited,  $\epsilon_{\text{H}_2\text{O}_{\text{t},3550}}$  is best described by  $\tau$  (Figure 5). We do not observe a strong relationship in the full dataset between  $\epsilon$  and  $\text{NBO}/\text{T}$ , calculated by the method outlined in Mysen and Richet [2018].

Dixon and Pan [1995] first demonstrated the dependence of  $\epsilon$  for  $\text{CO}_3^{2-}$  on  $\eta$ . The proportion of  $\text{Na}^+$  to  $\text{Ca}^{2+}$  modulates the dissolution of C as molecular  $\text{CO}_2$  and/or  $\text{CO}_3^{2-}$ . As the proportion of  $\text{Na}^+$  increases,  $\epsilon_{\text{CO}_3^{2-}}$  decreases (Figure 5). Carbon dissolves as both molecular  $\text{CO}_2$  and  $\text{CO}_3^{2-}$  in NaAl-rich sili-

cate glasses (albitic, jadeitic, nephelinitic compositions) [Mysen and Virgo 1980a; b; Fine and Stolper 1985; Dixon and Pan 1995], whereas carbon dissolves solely as  $\text{CO}_3^{2-}$  in Ca and CaMg-rich silicate glasses (diopsidic, sodamelilitic, and akermanitic compositions) [Fine and Stolper 1986; Dixon and Pan 1995].  $\epsilon_{\text{CO}_3^{2-}}$  data are often limited to either the  $\epsilon_{\text{CO}_3^{2-},1515}$  or  $\epsilon_{\text{CO}_3^{2-},1430}$  peak, which are also assumed to be approximately equal [Dixon and Pan 1995]. We parameterize a combined  $\epsilon_{\text{CO}_3^{2-}}$  with data from  $\epsilon_{\text{CO}_3^{2-},1515}$  and  $\epsilon_{\text{CO}_3^{2-},1430}$ , where available.

Uncertainties exist within both the compositional parameter ( $\tau$ ,  $\eta$ ) and molar absorptivity ( $\epsilon$ ). Higher uncertainties in compositional parameters may exist in older experimental studies where electron microprobe measurements quantified a limited number of oxide components. Variability in  $\epsilon$  can be attributed to differences in the baseline fitting method.  $\epsilon_{\text{H}_2\text{O}_{\text{m},5200}}$  and  $\epsilon_{\text{OH}^-_{4500}}$  have been quantified with both linear and Gaussian baselines, resulting in differences in the determined  $\epsilon$ . In order to account for uncertainties in our regression of  $\epsilon$  versus compositional parameter, we apply a variant of the inversion described in Chapter 9 of Menke [2018], with the implicit model:

$$f(x) = -y + m_0 + m_1 p = 0, \quad (7)$$

where  $m$  is the vector of coefficients to be solved,  $p$  is predictor variable or the compositional parameter,  $y$  is the dependent variable or the  $\epsilon$  value, and  $x$  is a vector containing  $\epsilon$ , compositional parameters, and the vector of coefficients. The inversion applies Newton's method for determining the minimum of a function in an inverse problem. The implicit inversion derives strength from the ability to incorporate experimental and compositional uncertainties into the calibration and to utilize information on the shape of the error for a trial solution to successively derive improved fits for model parameters, which minimize error. The full development and application of the implicit inversion technique is given in the Supplement, and the inversion code is available in the PyIRo-Glass GitHub repository.

We derive best-fit parameters and covariance matrices, evolving from the initial least squares fit to reach a minimum on the error surface, and compare these parameters against those from previous work (Figure 5). The problem is sufficiently overdetermined such that the solution does not depend significantly on the starting model and converges within 10 iterations. Best-fit compositional parameter multipliers ( $m_1$ ) increase and intercepts ( $m_0$ ) decrease for  $\epsilon_{\text{H}_2\text{O}_{\text{m},5200}}$ ,  $\epsilon_{\text{OH}^-_{4500}}$ , and  $\epsilon_{\text{H}_2\text{O}_{\text{m},1635}}$  from the previous parameterizations of Mandeville et al. [2002] and for  $\epsilon_{\text{CO}_3^{2-}}$  from Dixon and Pan [1995]. No previous parameterizations of  $\epsilon_{\text{H}_2\text{O}_{\text{t},3550}}$  exist. Variance within calibrated  $\epsilon$  differs significantly from the low variance  $\epsilon_{\text{H}_2\text{O}_{\text{m},5200}}$  and  $\epsilon_{\text{H}_2\text{O}_{\text{m},1635}}$  to high variance  $\epsilon_{\text{H}_2\text{O}_{\text{t},3550}}$ . The  $\epsilon_{\text{H}_2\text{O}_{\text{m},5200}}$  covariance matrix is small given low variance within the data. The  $\epsilon_{\text{H}_2\text{O}_{\text{m},1635}}$  covariance matrix is similarly small given few calibration data. The  $\epsilon_{\text{OH}^-_{4500}}$  covariance is slightly larger given higher variance within the data.  $\epsilon_{\text{H}_2\text{O}_{\text{m},3550}}$  variance is greater due to the increased variability in speciation due to quench temperatures

and quench rates.  $\epsilon\text{CO}_3^{2-}$  variance is similarly greater, particularly within the  $\epsilon\text{CO}_{3,1515}^{2-}$  calibrations, likely given convolution of the  $\text{H}_2\text{O}_{m,1635}$  and the  $\text{CO}_{3,1515}^{2-}$  tails.

Two forms of error—the error of calibration and the error of a single application of the inversion to molar absorptivity—can be quantified. We define the error of calibration as being equal to the posterior covariance in  $\epsilon$ , between the predicted and experimental  $\epsilon$ . The 68% confidence interval of a single application of the model incorporates the calibration uncertainty as well as the analytical uncertainty of the calculated compositional parameter, applied with:

$$c_T = Zc_m Z^T + mc_z m^T, \quad (8)$$

where  $Z$  is a vertical matrix of the measured compositional parameter,  $c_m$  is the diagonal posterior covariance on the model parameter coefficients,  $m$  is the vertical matrix of the posterior model parameter coefficients, and  $c_z$  is a diagonal matrix of the uncertainty of measured compositional parameter. We are thus able to derive  $\epsilon$  with a 68% confidence interval to account for both model and analytical uncertainty in a marked improvement to previous calibrations, where there are no estimates of the uncertainty of calibration. Application of the inversion with Equation 8 to the mid-ocean ridge basalt (MORB) composition of Dixon et al. [1995] with  $\tau=0.627$  predicts  $\epsilon\text{H}_2\text{O}_{m,5200} = 0.642 \pm 0.284$ ,  $\epsilon\text{OH}_{4500}^- = 0.583 \pm 0.264$ ,  $\epsilon\text{H}_2\text{O}_{m,1635} = 27.545 \pm 8.161$ , and  $\epsilon\text{H}_2\text{O}_{t,3550} = 60.524 \pm 7.088$  L/mol-cm. Application of the inversion to the Etna alkali basalt of Shishkina et al. [2014] with  $\eta=0.367$  predicts  $\epsilon\text{CO}_3^{2-} = 300.433 \pm 15.842$  L/mol-cm. Uncertainties associated with individual applications of the inversion are larger than those cited within the original studies, but more accurately capture the uncertainty of the model.

### 2.3 Calculating Thickness and Density

We develop an automated implementation for calculating thicknesses from reflectance spectra by the interference fringe method. Interference fringes are produced by the interactions between reflected light and reflections internal to the sample, with fringe wavelengths inversely proportional to thickness and proportional to refractive index of the sample [Nishikida et al. 1996; Tamic et al. 2001; Wysoczanski and Tani 2006; Sun et al. 2007]. Interference fringes from the reflectance spectra of two Volcán de Fuego olivines are shown in Figure 6. Nishikida et al. [1996] define the relationship applicable to glasses and olivine:

$$l = \frac{m}{2n(v_1 - v_2)}, \quad (9)$$

where  $l$  is the thickness of analyzed area,  $m$  is the number of fringes in the wavenumber range,  $n$  is the refractive index of the material, and  $v_1$  and  $v_2$  are the highest and lowest wavenumbers in the interval.

Signal-to-noise ratios associated with interference fringes in reflectance spectra can be low. Reflectance spectra are preprocessed with median filtering to remove potential single spike noise and successively processed with Savitzky-Golay filtering from the SciPy package [Virtanen et al. 2020], fitting low-degree polynomials to data with linear least squares, shown

in Figure 6 [Savitzky and Golay 1964]. Savitzky-Golay filtering improves signal quality by removing additional noise, but impacts peak amplitudes variably. Sinusoidal peaks with smooth extrema are not strongly impacted by filtering (Figure 6A), but peaks with sharp extrema are reduced in amplitude (Figure 6B). The locations of the peaks in filtered spectra, however, do not differ significantly despite the difference in amplitude. Local extrema associated with each interference fringe wave are located by identifying regions of greatest absorbance change. Maxima are surrounded by points that are lower in absorbance and minima are surrounded by points that are greater in absorbance. Individual local extrema identification by differentiation can fail with noisier spectra, but consideration of all peaks within the wavenumber range allows for uncertainty assessment. Thicknesses are calculated from the wavenumber differences ( $\lambda$ ) between all adjacent local extrema in the specified wavenumber range. Uncertainties in thickness are calculated from the standard deviation of all local maxima and minima-derived thicknesses. Individual thicknesses falling outside one standard deviation of the mean are removed.

Thicknesses from interference fringes in the wavenumber range of 2800 to 2000  $\text{cm}^{-1}$  were compared against those determined using a Mitutoyo 543-783B Digimatic Indicator for Volcán de Fuego olivines, to assess the uncertainty associated with this automated method. A refractive index of 1.709 was determined using the orientation- and forsterite-dependent parameterization of olivine refractive index from Howie et al. [1992] with a forsterite content of 72 (the mean composition measured next to the studied melt inclusions). Mean thicknesses calculated from interference fringes compare well with those from digital micrometer measurements (Figure 7). Agreement in thickness measurements is demonstrated by the high concordance correlation coefficient (CCC, a measurement of the agreement between two variables [Lin 1989]), low root-mean-square error (RMSE), low relative root-mean-square error (RRMSE), high coefficient of determination ( $R^2$ ), slope ( $m$ ) nearing 1, and intercept ( $b$ ) nearing 0. Mean thickness uncertainties from five repeat measurements are similar to previously reported values of less than 3  $\mu\text{m}$  [Nichols and Wysoczanski 2007; von Aulock et al. 2014; Allison et al. 2019].

Melt density is a function of glass composition and can be calculated from the gram formula weights and partial molar volumes, from Leshner and Spera [2015] or Iacovino and Till [2019], at ambient temperature and pressure of the analytical conditions at 25°C and 1 bar. The two models yield similar densities, differing by a maximum of 2% for the range of Volcán de Fuego melt inclusions. The large molar volume of  $\text{H}_2\text{O}$  significantly impacts density and requires the implementation of an iterative solver. Density is initially assumed to have no contribution from  $\text{H}_2\text{O}$  but is iteratively updated with the calculated amount of  $\text{H}_2\text{O}_{t,3550}$  or  $\text{H}_2\text{O}_{m,1635} + \text{OH}_{4500}^-$  if the sample is saturated (see Section 3.4). The density calculation is repeated to ensure stability and generally converges within 10 iterations.

Table 1:  $\epsilon$  calibration data for  $H_2O$  and  $CO_2$  species, including new linear molar absorptivities (peak amplitude-based) determined in this study for a series of synthetic basalts [Moussallam et al. 2024].  $\tau$  and  $\eta$  values recalculated from reported compositions. Additional information regarding the calculation of calibration uncertainties and the integrated molar absorptivities (peak area-based) are provided in the Supplement and PyIRoGlass GitHub repository.

Reference	Glass Composition	Analytical Method	$\tau$	$\epsilon_{H_2O_m,5200}$ (L/mol-cm)	$\epsilon_{OH^-}_{1500}$ (L/mol-cm)	$\epsilon_{H_2O_m,3550}$ (L/mol-cm)	$\epsilon_{H_2O_m,1635}$ (L/mol-cm)
Shishkina et al. [2014]	Nephelinite, E2624	KFT, EA	0.508			56.7	
Shishkina et al. [2014]	Basanite, A2549	KFT, EA	0.532			57.3	
Shishkina et al. [2014]	Alkali basalt, B2518	KFT, EA	0.585			60.3	
Shishkina et al. [2014]	Alkali basalt, B2507	KFT, EA	0.585			60.5	
Mercier et al. [2010]	Basanite	KFT	0.588			43.96	
Aoccella et al. [1984]	$Na_2O^*3SiO_2$	Experimental Loading	0.600	0.634	0.267		
Lesne et al. [2011]	Basalt (Vesuvius)	KFT	0.607	0.57	0.7		
Behrens et al. [2009]	Ultrapotassic melt	KFT, EA	0.622	1.02	0.62	63.9	
Dixon et al. [1995]	MORB	Manometry	0.627	0.62	0.67	63	25
Ohlhorst et al. [2001]	Basalt	KFT	0.629	0.66	0.57		
Lesne et al. [2011]	Basalt (Stromboli)	KFT	0.630	0.62	0.97		
Lesne et al. [2011]	Basalt (Etna)	KFT	0.631	0.56	0.75		
Stolper [1982]	Basalt SLNT	Manometry	0.636			64	
Stolper [1982]	Basalt Bouvet CHN	Manometry	0.639			72	
Pandya et al. [1992]	Basalt	Mass Spectrometry	0.643			61	
Jendrzewski et al. [1997]	MORB	Manometry	0.645			78	
Shi et al. [2024], this study	Basalt	ERDA, SIMS	0.646			63.03	
Vetere et al. [2011]	Shoshonite	KFT	0.659	1.03	0.8		
Di Matteo et al. [2006]	Shoshonite	KFT	0.663			60	
Shishkina et al. [2010]	Basalt	KFT, EA	0.664	0.65	0.69	65	
Shishkina et al. [2010]	Basalt	KFT, EA	0.664	0.65	0.69	65	
Yamashita et al. [1997]	Tholeiite	Manometry	0.665	0.84	0.85	64	
Mercier et al. [2010]	Basalt	KFT	0.666			62.8	
Stolper [1982]	Basalt Marianas 46D-1-1	Manometry	0.668			67	
Yamashita et al. [1997]	High Al Basalt	Manometry	0.671	0.84	0.85	64	
Fiège et al. [2015]	Mg-poor basalt	KFT	0.689	0.848	1.161		
Stolper [1982]	Basalt Tasaday	Manometry	0.691			75	
Jakobsson [1997]	Icelandite	EA	0.708	1.25	0.95		42
Di Matteo et al. [2006]	Latite	KFT	0.712			60	
Carroll and Blank [1997]	Phonolite	Manometry	0.720	1.10	1.25		
Ohlhorst et al. [2001]	Andesite	KFT	0.722	0.90	0.77		
King et al. [2002]	Andesite	Manometry, SIMS	0.743	1.08	1.15	70.3	40.8
Mandeville et al. [2002]	Fe-Bearing Andesite	Manometry	0.746	1.07	0.79	62.32	42.34
Di Matteo et al. [2004]	Trachyte	KFT	0.755	1.36	1.58		
Vetere et al. [2006]	Fe-Free Andesite	KFT	0.756	1.04	0.92		
Silver et al. [1990]	Jadeite Glass	Manometry	0.756	1.13	1.12		
Silver et al. [1990]	CAS-E2	Manometry	0.774	1.07	0.85		
Yamashita et al. [1997]	Dacite	Manometry	0.782	1.60	0.94	68	
Ohlhorst et al. [2001]	Dacite	KFT	0.783	1.17	1.02		
Allabar and Nouak [2020]	Peralkaline rhyolite	KFT	0.791	1.20	1.5		
Mandeville et al. [2002]	Fe-Free Andesite	Manometry	0.795	1.46	0.89	69.21	52.05
Withers and Behrens [1999]	Albite, 300 K	KFT	0.797	1.47	1.27		
Silver et al. [1990]	Orthoclase, KAS	Manometry	0.799	1.87	1.43		
Behrens [1995]	Albite	KFT	0.799	1.49	1.28		
Silver and Stolper [1989]	Albite	Manometry, NMR	0.799	1.67	1.13	70	49
Behrens et al. [1996]	Orthoclase, K100	KFT	0.806	1.65	1.58		
Stolper [1982]	Hydrated Obsidian OBS G	Manometry	0.811			55	
Stolper [1982]	Hydrated Obsidian OBS I	Manometry	0.813			66	
Stolper [1982]	Hydrated Obsidian OBS E	Manometry	0.813			73	
Nouak and Behrens [1995]	Haplogranite	KFT	0.850		1.56		
Stabile et al. [2020]	Pantellerite	KFT	0.853		0.99		
Leschik et al. [2004]	Rhyolite	KFT	0.856			80	
Withers and Behrens [1999]	Rhyolite	KFT	0.856	1.69	1.47		
Neuman et al. [1986]	Rhyolite	Manometry	0.859	1.61	1.73	100	55
Hauri et al. [2002]	Rhyolite	SIMS	0.859			90	56
Okumura and Nakashima [2005]	Rhyolite	KFT	0.860	1.75	1.42		
Ihinger et al. [1994]	Rhyolite	Manometry	0.860	1.86	1.5	80	55
Aubaud et al. [2009]	Rhyolite	ERDA	0.860			95	
Okumura et al. [2003]	Rhyolite	KFT	0.864			75	
Silver et al. [1990]	Rhyolite	Manometry	0.864	1.61	1.73		
Dobson et al. [1989]	Rhyolite	Manometry	0.867			88	
Stolper [1982]	Synthetic Albite A78-56	Manometry	0.902			88	

Reference	Glass Composition	Analytical Method	$\eta$	$\epsilon_{CO_2^{2-}}_{3,1515}$ (L/mol-cm)	$\sigma\epsilon_{CO_2^{2-}}_{3,1515}$ (L/mol-cm)	$\epsilon_{CO_2^{2-}}_{3,1430}$ (L/mol-cm)	$\sigma\epsilon_{CO_2^{2-}}_{3,1430}$ (L/mol-cm)
Behrens et al. [2009]	Ultrapotassic	KFT, EA	0.2316	308	110		
Shi et al. [2024], this study	Basalt	NRA	0.2356	303.44	9.20	303.44	9.20
Vetere et al. [2014]	Phonotephrite AH1	KFT, EA	0.2369			294	16
Jendrzewski et al. [1997]	MORB	Manometry	0.2446	398	10	398	10
Bronce et al. [2021]	Boninite	EA	0.2630			265	30
Dixon and Pan [1995]	Basanite	EA	0.2680	284	5	281	6
Fine and Stolper [1986]	Basalt	NRA	0.2680	375	20	375	20
Shishkina et al. [2014]	MORB, 169oxi	KFT, EA	0.2755	359	25	306	11
Shishkina et al. [2010]	Basalt	KFT, EA	0.2766	361	43	317	23
Thibault and Houlouay [1994]	Leucite	SIMS	0.2883	355		355	
Shishkina et al. [2014]	Ferro-basalt, SC1	KFT, EA	0.3028	372	14	329	15
Shishkina et al. [2014]	Basanite, A2549	KFT, EA	0.3610	349	25	306	32
Shishkina et al. [2014]	Alkali basalt, OB93	KFT, EA	0.3669	385	18	341	19
Shishkina et al. [2014]	Alkali basalt, Etna	KFT, EA	0.3670	394	27	360	24
Shishkina et al. [2014]	Alkali basalt, B2507	KFT, EA	0.3912	380	30	311	41
Vetere et al. [2014]	Phonotephrite AH2	KFT, EA	0.4241			244	15
Vetere et al. [2011]	Shoshonite	KFT, EA	0.4384			356	18
Jakobsson [1997]	Icelandite	EA	0.5074	180	15	190	15
Vetere et al. [2014]	Phonotephrite AH3	KFT, EA	0.5369			264	15
Vetere et al. [2014]	Latite	KFT, EA	0.5903			215	8
Duncan and Dasgupta [2015]	Rhyolite	SIMS	0.8406	207	22	143	10



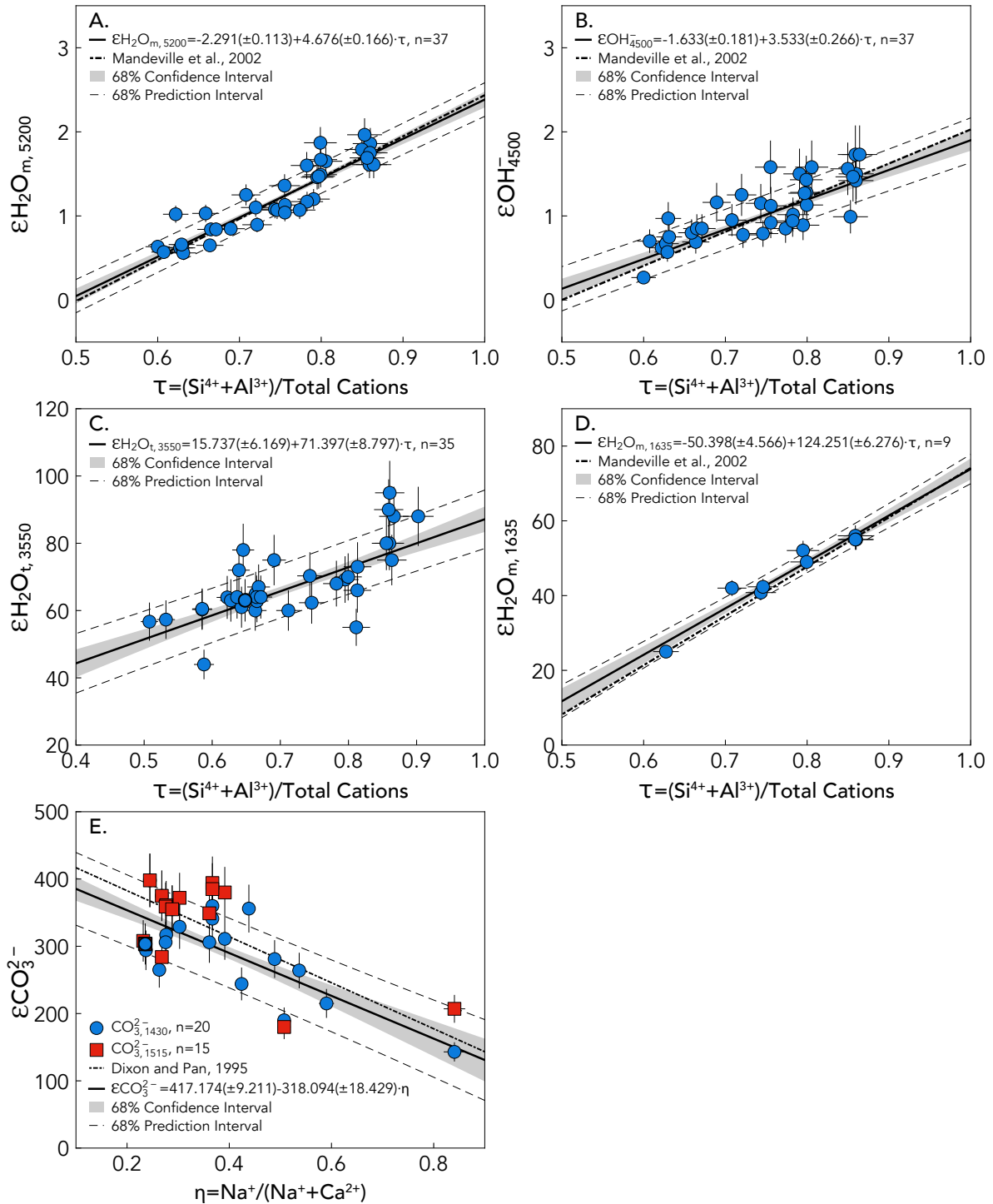


Figure 5: Tetrahedral cation fraction  $\tau = (\text{Si}^{4+} + \text{Al}^{3+})/\text{total cations}$  against: A.  $\epsilon_{\text{H}_2\text{O}_{\text{m},5200}}$ . B.  $\epsilon_{\text{OH}_{4500}^-}$ . C.  $\epsilon_{\text{H}_2\text{O}_{\text{t},3550}}$ , with the new calibrated  $\epsilon_{\text{H}_2\text{O}_{\text{t},3550}} = 63.03 \pm 4.47$  L/mol-cm demarcated by the bold scatter symbol. See Section 2.1 (Table 1 and Figure 1) of the Supplement for additional information on calibration. D.  $\epsilon_{\text{H}_2\text{O}_{\text{m},1635}}$ . E. Cation fraction  $\eta = \text{Na}^+ / (\text{Na}^+ + \text{Ca}^{2+})$  against  $\epsilon_{\text{CO}_3^{2-}}$ , with the new calibrated  $\epsilon_{\text{CO}_3^{2-}_{3,1515,1430}} = 303.44 \pm 9.20$  L/mol-cm demarcated by the bold scatter symbol. See Section 2.1 (Table 1 and Figure 1) of the Supplement for additional information on calibration.

2.4 PylRoGlass: An MCMC Algorithm for Calculating Volatile Concentrations with Uncertainties

fitting range from 2400 to 1250  $\text{cm}^{-1}$ , is expressed in the following form:

520 The net equation describing the absorbance spectrum of a glass or melt inclusion, with  $\nu^-$  defined as the wavenumber



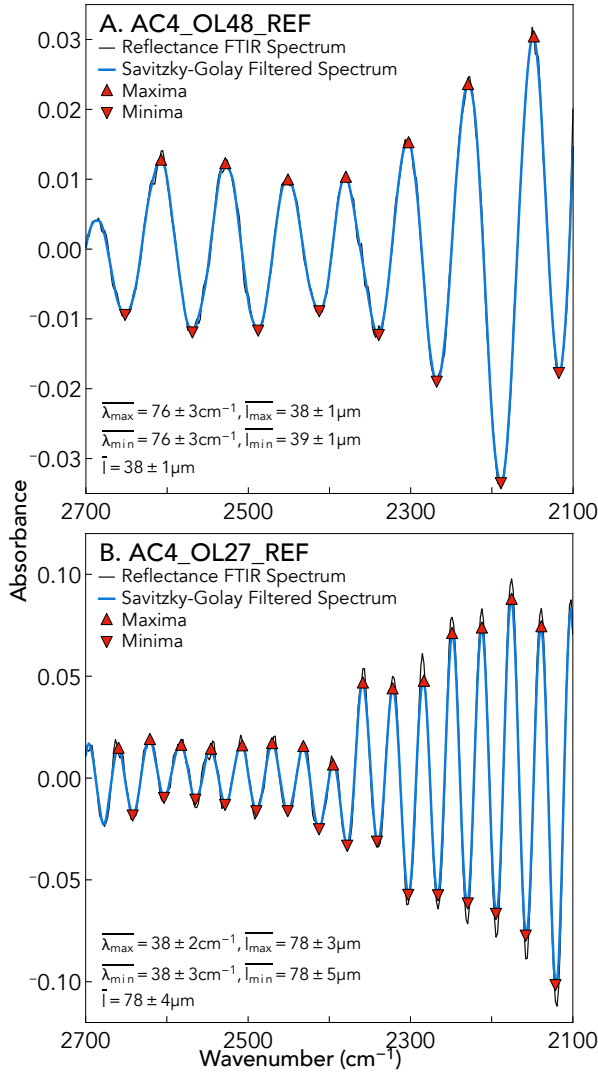


Figure 6: Reflectance FTIR spectra with interference fringes for olivines from Volcán de Fuego, Guatemala. The relationship between wavenumber differences ( $\lambda$ ) and wafer thickness is negative, as larger differences are associated with lower thicknesses. A. Olivine wafer VF18-AC4-OL48 (black) with Savitzky-Golay smoothed spectrum (blue) and identified extrema (red triangles). OL48 spectrum and filtered spectrum are sinusoidal and smooth, with strong agreement between the raw and smoothed spectra. B. Olivine wafer VF18-AC4-OL27 with initially sharp, singular peaks; Savitzky-Golay smoothed spectrum has reduced amplitudes. Local extrema wavenumbers locations remain well reproduced. Local extrema are more closely spaced than those from OL48, thus OL27 is thicker.

$$\hat{A} = x_0 \overline{B} + x_1 \overline{B}_{PC1} + x_2 \overline{B}_{PC2} + x_3 \overline{B}_{PC3} + x_4 \overline{B}_{PC4} + y_0 \overline{H_2O_{m,1635}} + y_1 \overline{H_2O_{m,1635}PC1} + y_2 \overline{H_2O_{m,1635}PC2} + \frac{a_{1515}}{2\sigma_{1515}^2} \cdot e^{-(v - \mu_{1515})^2} + \frac{a_{1430}}{2\sigma_{1430}^2} \cdot e^{-(v - \mu_{1430})^2} + mv + b \quad (10)$$

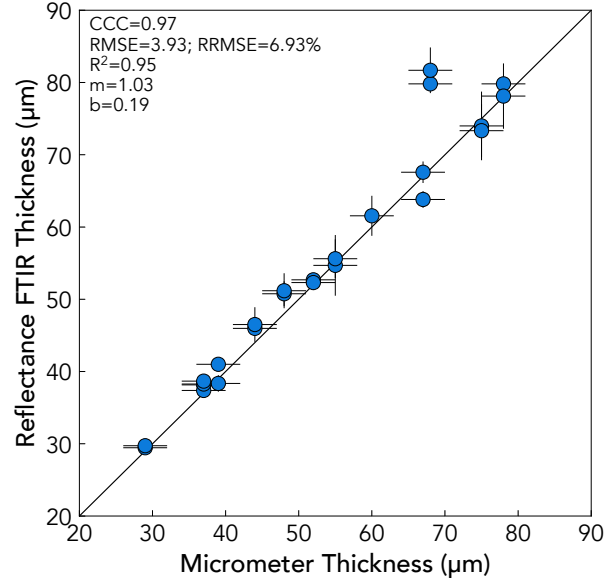


Figure 7: Thicknesses from interference fringes of FTIR spectra compared to those from digital micrometer. Uncertainties on interference fringe thicknesses are calculated from the standard deviation of all maxima- and minima-derived thicknesses within the wavenumber range of 2800 to 2000  $\text{cm}^{-1}$ . Uncertainties on thicknesses from the digital micrometer are set at the stated uncertainty of 3  $\mu\text{m}$ . Agreement between calculated and measured thicknesses is indicated by high CCC, low RMSE ( $\mu\text{m}$  unit) and RRMSE (unitless), high  $R^2$ ,  $m$  nearing 1, and  $b$  nearing 0.

where  $x_0, x_1, x_2, x_3, x_4, y_0, y_1, y_2, a_{1515}, a_{1430}, \sigma_{1515}, \sigma_{1430}, \mu_{1515}, \mu_{1430}, m$ , and  $b$  are the best-fit coefficients or parameters.  $x_n$  and  $y_n$  describe best-fit coefficients for the mean baseline or peak and the principal components associated with the baseline or peak. The remaining variables describe best-fit parameters.

Table 2: PyIRoGlass coefficients and parameters in Equation 10.

Abbreviation	Coefficient or Parameter
$\overline{B}$	Mean volatiles below detection baseline
$\overline{B}_{PCn}$	$n$ -th principal component of baseline
$x_n$	Best-fit coefficient for baseline-related terms
$\overline{H_2O_{m,1635}}$	Mean $H_2O_{m,1635}$ peak
$\overline{H_2O_{m,1635}PCn}$	$n$ -th principal component of $H_2O_{m,1635}$ peak
$y_n$	Best-fit coefficient for $H_2O_{m,1635}$ -related terms
$a_{1515/1430}$	$\text{CO}_3^{2-}$ peak amplitude
$\mu_{1515/1430}$	$\text{CO}_3^{2-}$ peak center
$\sigma_{1515/1430}$	$\text{CO}_3^{2-}$ peak half-width
$v^-$	Wavenumber fitting range
$m$	Slope of linear tilt
$b$	Intercept of linear tilt

These best-fit coefficients or parameters are first initialized with ordinary least squares. The parameter space of

the modeled absorbance of the transmission FTIR spectrum is sampled and explored by leveraging a Markov Chain Monte Carlo sampler in a Bayesian parametric framework, to account for uncertainty. In this framework of Bayesian inference, the posterior joint probability distribution of model parameters is quantified as a function of the prior probability of model parameters and a likelihood function. Bayes' Theorem dictates that the posterior joint probability distribution is updated as more information becomes available, following Cubillos et al. [2017]:

$$P(\theta|y, M) \propto P(\theta|M)P(y|\theta, M), \quad (11)$$

where  $y$  denotes data,  $\theta$  is the set of parameters,  $M$  is the credible region for the set of model parameters,  $P(\theta|M)$  is the prior probability distribution (not incorporating new information),  $P(y|\theta, M)$  is the likelihood, and  $P(\theta|y, M)$  is the posterior probability distribution of parameters. The prior probability distribution of parameters is defined by the expected range and distributions of these parameters. The likelihood serves as the probability density function of the modeled data, given an array of parameters. A Markov Chain Monte Carlo (MCMC) algorithm was utilized to generate random samples from the parameter space that hold a probability density distribution that is proportional to the posterior probability distribution. The MCMC approach utilizes a series of jumps between samples, to effectively traverse and explore parameter space. The open-source Python package, Multi-Core Markov Chain Monte Carlo (MC<sup>3</sup>), developed by Cubillos et al. [2017] integrates these statistical methods and was implemented for this study.

Fixed absorbance spectra provide the information required to refine posterior probability distributions of model parameters. Prior probability distributions describing the baseline, peaks, and lines can be characterized using either uniform or Gaussian distributions. Uniform priors assign equal probabilities across their defined range, making all values equally probable. In contrast, Gaussian priors assign probabilities based on a Gaussian probability distribution, characterized by its mean and standard deviation. Priors for the parameters relating to the baseline and H<sub>2</sub>O<sub>m</sub> peak are bounded by the range of variability in principal component space, when the principal component vectors are fit back to PCA space; this is akin to a linear transform from wavenumber to principal component space. These initial priors were limited after testing with the test dataset of Section 3.2 to avoid overfitting. Parameters related to the baseline, H<sub>2</sub>O<sub>m</sub> peak, CO<sub>3</sub><sup>2-</sup> doublet peak amplitudes, and linear adjustment are sampled uniformly due to the larger variability in these parameters in the absence of *a priori* knowledge. Priors for the CO<sub>3</sub><sup>2-</sup> doublet peak locations and half-widths are constrained by prior knowledge about this peak. The CO<sub>3</sub><sup>2-</sup> doublet peak locations and half-widths are defined with Gaussian priors, reflecting the well-established nature of these parameters in the absorbance spectra of basaltic to andesitic glasses. The initial parameters for these priors are optimized with the least squares Trust Region Reflective algorithm, which is particularly suited for well-constrained, large problems [Branch et al. 1999].

We implement PyIRoGlass using 10<sup>6</sup> samples, 9 chains, and 2 · 10<sup>4</sup> burn-in samples. We employ the Snooker Updater Differential Evolution Markov Chain method (DEMC) for random MCMC sampling [ter Braak 2006; ter Braak and Vrugt 2008]. In the Snooker Updater DEMC algorithm,  $N$  chains are computed in parallel. The algorithm computes the differences between the chain from which the jump is being proposed and the remaining chains ( $N - 1$ ), utilizing the differences to determine the scale and orientation of each proposed jump [ter Braak and Vrugt 2008]. The chains converge towards a posterior distribution, ensuring that evolution is oriented and scaled appropriately. We apply a Gelman-Rubin convergence criterion with a threshold of 1.01 to assess convergence. The Gelman-Rubin convergence criterion determines differences both within and across chains. When the variance between chains is minimal, the Gelman-Rubin convergence criterion should approach 1, indicating that the chains have effectively converged to the posterior distribution [Gelman and Rubin 1992]. The MCMC will thus terminate early. The Snooker Updater DEMC optimizes acceptance rates and efficiency. Processing a single transmission spectrum and generating all output files takes approximately 20 seconds on a M2 Max MacBook Pro with 12 CPU cores. The same task takes about 2 minutes on the cloud-based Python development environment of Google Colab.

PyIRoGlass calculates volatile concentrations with their associated uncertainties using a final MCMC scheme with all parameters in the Beer-Lambert Law. ALS (Section 2.1.1) and MC<sup>3</sup> baseline-derived peak amplitudes (Section 2.1.2) are used to determine concentrations of H<sub>2</sub>O and CO<sub>2</sub> species, with glass composition used to determine the composition-dependent  $\epsilon$  (Section 2.2) and to iteratively determine density (Section 2.3), all as a function of sample thickness (Section 2.3). The best-fit peak amplitudes, molar absorptivities, thicknesses, and densities are applied in the Beer-Lambert Law to determine the concentration of each peak. The uncertainty associated with each concentration is taken by running a simple Monte Carlo error assessment in which all parameters, except molar mass, are allowed to vary with Gaussian distributions for 5 · 10<sup>5</sup> samples.

## 3 APPLICATION AND VALIDATION OF PYIROGLASS

### 3.1 PyIRoGlass Structure and Packaging

#### 3.1.1 Installation

PyIRoGlass can be locally installed with Python versions 3.8-3.12 through the command line:

```
1 pip install PyIRoGlass
```

We further provide a cloud-based Python development environment in Google Colab, with links provided on the PyIRoGlass GitHub repository. These implementations create interactive computing environments without necessitating local installations of Python. In these cloud-based Python development environments, installation instead occurs within a code cell:

```
1 !pip install PyIRoGlass
```

Following installation, the PyIRoGlass package must then be imported and initialized with:

```
1 import PyIRoGlass as pig
```

645 Functions from PyIRoGlass are then called with the abbreviated package name, followed by the function name. The primary functions required for processing transmission FTIR spectra with PyIRoGlass include the classes and method functions for loading spectra and/or chemistry and thickness data, and functions calculating baselines and calculating concentrations. 650 The `load_spectrum_directory` method in the `SampleDataLoader` class identifies and loads all FTIR spectra within a directory into a dictionary and is called as follows:

```
1 loader = pig.SampleDataLoader(args)
655 2 loader.load_spectrum_directory()
```

The `load_chemistry_thickness` method in the `SampleDataLoader` class loads chemistry and thickness data and is called as follows:

```
1 loader = pig.SampleDataLoader(args)
660 2 loader.load_chemistry_thickness()
```

Alternatively, both the directory of FTIR spectra and file with chemistry and thickness data can be loaded simultaneously with the `load_all_data` method in the `SampleDataLoader` class as follows:

```
665 1 loader = pig.SampleDataLoader(args)
2 loader.load_all_data()
```

The function then calculating baselines for each FTIR spectrum in the dictionary is called as follows:

```
1 pig.calculate_baselines(args)
```

670 and the function calculating concentrations from the peak amplitudes returned from the `calculate_baselines` function is called as follows:

```
1 pig.calculate_concentrations(args)
```

All functions require the input of specific variables within the parentheses, called arguments (abbreviated to args).

The additional function for processing reflectance FTIR spectra identifies peak and trough locations and determines thicknesses. The `SampleDataLoader` class and associated methods are reused for loading reflectance FTIR spectra. The function determining all thicknesses is called as follows:

```
1 pig.calculate_mean_thickness(args)
```

685 The PyIRoGlass code is actively maintained on GitHub, where the most recent version and full development history are readily accessible in the repository. The current stable PyIRoGlass release (Version 0.6.1) with all code, documentation, and data, has been archived on Zenodo with a static DOI (10.5281/zenodo.10883628). All available functions and arguments can be accessed and explored in the PyIRoGlass Read the Docs ([pyiroglass.readthedocs.io](http://pyiroglass.readthedocs.io)). The cloud-based Python development environments are recommended for ease of use for Python beginners, but significant computational gains are provided by running the code locally.

### 3.1.2 Data Input

The two required types of input files include FTIR spectrum files and the chemistry and thickness file. Each FTIR spectrum is input as a CSV file, unmodified from the Thermo Scientific Nicolet iN10 MX Fourier Transform Infrared Spectrometer outputs, with a wavenumber and absorbance column. The chemistry and thickness file is structured as a CSV file with columns with headers: Sample, SiO<sub>2</sub>, TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, FeO, MnO, MgO, CaO, Na<sub>2</sub>O, K<sub>2</sub>O, P<sub>2</sub>O<sub>5</sub>, Thickness, and Sigma\_Thickness. Sample input files are provided in the PyIRoGlass GitHub repository.

### 3.1.3 Code Input

Computational workflow examples for PyIRoGlass are provided in the Google Colab run file example on the PyIRoGlass GitHub repository. The workflow is structured such that the sole modifications required are for the paths to input files, shown as follows:

```
1 import os
2 spectrum_path = os.path.join(os.getcwd(), 'Inputs/
TransmissionSpectra')
3 chemistry_thickness_path = os.path.join(os.getcwd(), 'Inputs/
ChemThick.csv')
4 export_path = os.path.join(os.getcwd(), 'Outputs')
```

These lines of code are used to navigate to the paths of directories and files. In this case, we have a directory called PyIRoGlass with the primary code run file (where this code would be found) and a directory called Inputs. The Inputs directory contains a sub-directory of transmission FTIR spectra and a CSV of chemistry and thickness data. The sub-directory is called TransmissionSpectra and contains the transmission FTIR spectra of interest, which can be batched and run at the same time. One additional file containing chemistry and thickness data for all the spectra of interest is called 'ChemThick.csv'. The following functions within PyIRoGlass are used to load and read these files as Python dictionaries or dataframes.

```
1 loader = pig.SampleDataLoader(spectrum_path=spectrum_path,
chemistry_thickness_path=chemistry_thickness_path)
2 dfs_dict, chemistry, thickness = loader.load_all_data()
```

The spectra can then be batch processed through PyIRoGlass with the saved outputs:

```
1 peak_amplitude_df, failures = pig.calculate_baselines(dfs_dict,
export_path)
2 concentrations = pig.calculate_concentrations(peak_amplitude_df,
chemistry, thickness, export_path)
```

The `calculate_baselines` function, fitting baselines to all spectra, takes the arguments of a dictionary of transmission FTIR spectra and a string with the export path and returns the `peak_amplitude_df` dataframe. All parameters—most importantly, peak amplitudes with uncertainties—sampled from the MC<sup>3</sup> and ALS fitting of all species peaks are returned within the `peak_amplitude_df` dataframe. The `calculate_concentrations` function, calculating concentrations from peak amplitudes, takes the arguments of a dataframe with peak amplitudes and uncertainties, a dataframe with sample chemistry, a dataframe with sample thickness, and a string with the export path. `calculate_concentrations` returns

the concentrations dataframe which contains volatile concentrations with uncertainties, peak saturation information, signal-to-noise-ratios, density, and molar absorptivities. Both dataframes are saved for future reference.

### 3.1.4 Data and File Output

PyIRoGlass returns six forms of outputs: dataframes (.csv) including volatile concentrations with uncertainties, peak amplitudes, densities, and molar absorptivities; figures (.pdf) of peak fits, histograms of explored parameter space, pairwise plots of explored parameter space, and trace plots of explored parameter space; log (.log), text (.txt), zipped (.npz) files recording explored parameter space and statistics; pickle (.pkl) files containing best-fit baselines. We will walk through one instance of PyIRoGlass and show the output files in Section 3.3. Additional examples of output files are provided in the PyIRoGlass GitHub repository.

### 3.1.5 Unit Testing

To ensure the reliability and robustness of the PyIRoGlass package for FTIR spectra processing, we implemented a comprehensive suite of unit tests. Unit tests are a foundational component of software development. The primary objective of unit tests is to validate that each function in the package works as expected and to detect potential regressions during development as new features are added, modifications are made, or package versions are updated. We develop unit tests for most functions within the code:

- Data Loading:** Ingest data to ensure consistent format for package integration.
- Fitting Functions:** Validate Markov Chain Monte Carlo outputs of VF18-AC4-OL49 and VF18-AC4-OL53 for peak amplitude consistency up to the third decimal, permitting some variability within the sampling regime. Confirm ALS-derived peak amplitudes for consistency up to the fifth decimal. Ensure creation of output directories and files.
- Concentration, Density, Epsilon Calculations:** Cross-check algorithms against select samples with variable glass compositions, for both saturated and unsaturated transmission FTIR spectra. Ensure that volatile concentrations agree up to the fifth decimal place and that Monte Carlo errors agree within 0.01 wt.% for H<sub>2</sub>O and 1 ppm for CO<sub>2</sub>.
- Thickness Calculations:** Assess the agreement in thicknesses derived from interference fringes of reflectance FTIR up to the fifth decimal.
- Plotting:** Implement tests to ensure plots are generated accurately and consistently.
- Inversions:** Examine Newtonian inversions for molar absorptivity to ensure correct determinations of fitting parameters and uncertainties to the fifth decimal.

We utilize the pytest package and framework for executing tests [Krekel et al. 2004]. The choice of pytest was motivated by its widespread adoption in the Python community,

and its flexibility in handling test scenarios. At each instance of modification to the package code, the unit tests are automatically executed within GitHub Workflows. This ensures that the performance and integrity of the software remains intact with every change. Our unit testing currently covers 94% of the PyIRoGlass's code. This provides a quantifiable metric of how much of the software's functionality is tested automatically for reproducibility. Through this extensive and tailored test suite, we aim to capture potential anomalies, inaccuracies, or failures in the spectrum processing pipeline, ensuring PyIRoGlass's reliability across its breadth of functionalities.

## 3.2 Volcán de Fuego Melt Inclusions: A Validation Dataset

We demonstrate the performance of PyIRoGlass with a validation dataset of melt inclusions from the 2018 eruption of Volcán de Fuego, Guatemala. This exercise underscores the variable quality of output peak information. Samples consist of Aguas Calientes (AC4, IGSN: TAP000081) tephra fall deposits from the largest ash plume of the Volcán de Fuego eruption of June 3, 2018. These samples are the focus of a study currently underway [Shi et al. 2021]. Natural glass standards and olivine-hosted melt inclusions (MIs) were analyzed with the Thermo Scientific Nicolet iN10 MX Fourier Transform Infrared Spectrometer at the Lamont-Doherty Earth Observatory. Dry and CO<sub>2</sub>-scrubbed air purged the machine and measurements were made on a liquid nitrogen-cooled MCT-A detector. Our methodology for preparing samples and analyzing melt inclusions by FTIR is further described in the Supplement. Periodic internal check standard analyses of back-arc basin glass D1010 and melt inclusions CN-C-OL1', CN92C-OL2, and ETF46 were performed through each analytical session, as in-house check standards. We found it to be good practice to measure these check standards regularly to ensure data quality.

## 3.3 Volcán de Fuego Melt Inclusions: Parameter Posteriors and Spectrum Fits

Posterior distributions from one application of PyIRoGlass inform our understanding of the relationships between parameters and their underlying uncertainties. Figure 8 shows the parameter posterior probability density distributions, when applied to melt inclusion VF18-AC4-OL49. Strong correlations exist between the posterior probabilities of the baseline-generating coefficients of  $x_0$  scaling  $\bar{B}$ ,  $x_1$  scaling  $\bar{B}_{PC1}$ ,  $x_2$  scaling  $\bar{B}_{PC2}$ ,  $x_3$  scaling  $\bar{B}_{PC3}$ ,  $x_4$  scaling  $\bar{B}_{PC4}$ ,  $m$ , and  $b$ . This suggests that there is non-uniqueness in the sampled best-fit solutions, resulting in a strong positive covariance structure between  $x_0$ ,  $x_1$ , and  $x_3$ , as well as a negative covariance structure between  $x_0$ ,  $x_2$ , and  $x_4$ . The posterior probabilities of  $m$  and  $b$  are strongly negatively correlated, which further highlights the non-unique balance between parameters.

The posterior probabilities of the parameters fitting the CO<sub>3</sub><sup>2-</sup> doublet reveal positive correlations in the peak-amplitude related,  $a_{1515}$  and  $a_{1430}$ . This indicates that the CO<sub>3</sub><sup>2-</sup> doublet peaks should possess similar amplitudes, consistent with the assumptions of Dixon and Pan [1995]. The coefficients,  $y_n$ , which fit the H<sub>2</sub>O<sub>m,1635</sub> peak are correlated



with the parameters fitting the  $\text{CO}_3^{2-}$  peak, which is expected given the proximity of the peaks and potential convolution of the tails. The peak amplitude modulating coefficient,  $y_0$ , for  $\text{H}_2\text{O}_{\text{m},1635}$  shows no correlation with the parameters fitting the  $\text{CO}_3^{2-}$  peak. The peak position modulating coefficients,  $y_1$  and  $y_2$ , respectively show positive and negative correlations with  $\sigma_{1515}$ , the parameter controlling the half-width of the  $\text{CO}_3^{2-}$  peak; the . These findings underscore the importance of accounting for covariance between coefficients and parameters in ensemble Bayesian frameworks when fitting baselines and peaks to FTIR spectra, especially for accurately assessing volatile concentration uncertainties.

Figure 9 shows the resulting baseline and peak fits from PyIRoGlass for melt inclusion VF18-AC4-OL49, which is also the subject of Figure 1 and of the unit testing described in Section 3.1.5. The melt inclusion is saturated in  $\text{H}_2\text{O}_{\text{t},3550}$ , given the ragged peak and absorbance exceeding 2, resulting in the need to combine  $\text{H}_2\text{O}_{\text{m},1635}$  and  $\text{OH}_{4500}^-$  to quantify  $\text{H}_2\text{O}_{\text{t}}$  (Figure 9A). We sample the uncertainty in near-infrared peak amplitude by fitting three ALS baselines with variable wavenumber fitting ranges to the  $\text{H}_2\text{O}_{\text{m},5200}$  and  $\text{OH}_{4500}^-$  peaks (Figure 9B). The baseline-subtracted  $\text{H}_2\text{O}_{\text{m},5200}$  and  $\text{OH}_{4500}^-$  peaks are then interpolated with kriging to reduce noise within the peaks (Figure 9C), and quantify the maximum peak amplitude [Krige 1951; Cressie 1990]. Variability within the smoothed peak amplitudes is observed, given uncertainty in the fitting ranges for these peaks. Both near-infrared peaks have signal-to-noise ratios exceeding 4, representing meaningful signals. The  $\text{H}_2\text{O}_{\text{t},3550}$  peak is similarly fit with three ALS baselines and median filtered to reduce single spike noise (Figure 9D). The peak is not used in this sample given saturation and the introduction of non-linearity to the Beer-Lambert Law. Baseline and peaks, fit simultaneously, for the  $\text{H}_2\text{O}_{\text{m},1635}$  peak and  $\text{CO}_3^{2-}$  doublet are generated and sampled through  $10^6$  iterations (Figure 9E). The peak amplitudes and concentrations for both peaks in the  $\text{CO}_3^{2-}$  doublet are near identical. We report  $\text{CO}_2$  as the mean of the  $\text{CO}_3^{2-}$  doublet peaks. The PyIRoGlass fit to this transmission FTIR spectrum sees residuals in absorbance of less than 0.01 in the region of interest beneath the  $\text{H}_2\text{O}_{\text{m},1635}$  peak and  $\text{CO}_3^{2-}$  doublet. The combination of the Bayesian framework and fitting technique allows for robust determinations of both volatile concentrations and their uncertainties.

### 3.4 Observations on $\text{H}_2\text{O}$ Species Peak Quality

The derivation of concentrations from the  $\text{H}_2\text{O}_{\text{m},1635}$  and  $\text{H}_2\text{O}_{\text{m},5200}$  peaks prompts the question of their relative quality and performance. We determine  $\text{H}_2\text{O}$  species concentrations with PyIRoGlass to compare the  $\text{H}_2\text{O}_{\text{m}}$  peaks in the validation dataset of Volcán de Fuego melt inclusions and the internal check standards noted above (Figure 10, Section 3.2). The Volcán de Fuego melt inclusions form the primary basis of this analysis, given the composition- and matrix-matching of the samples. Repeated measurements of the internal check standards allows for assessment of variability in the  $\text{H}_2\text{O}_{\text{m},1635}$  and  $\text{H}_2\text{O}_{\text{m},5200}$  peaks through time. Triplicate analyses of internal check standards were made through each of the 12 analytical sessions, periodically spaced through the session.

Both datasets are filtered to only contain analyses where near-infrared peaks have signal-to-noise ratios exceeding 4.

$\text{H}_2\text{O}_{\text{m},5200}$  primarily predicts concentrations greater than those from  $\text{H}_2\text{O}_{\text{m},1635}$  in the Volcán de Fuego melt inclusions (Figure 10A) and internal check standards (Figure 10B, see Section 3.5 and Table 4). Most analyses fall above the 1-1 line and the slopes fit to the datasets exceed 1. Two clusters of internal check standards—back-arc basin glass D1010 ( $\text{H}_2\text{O}_{\text{m},1635} \sim 0.15$  wt.%) and Cerro Negro melt inclusion CN92C-OL2 ( $\text{H}_2\text{O}_{\text{m},1635} \sim 2.60$  wt.%)—highlight the variability observed in the  $\text{H}_2\text{O}_{\text{m},5200}$  peak. Concentrations from the  $\text{H}_2\text{O}_{\text{m},1635}$  peak are tightly constrained, while concentrations from the  $\text{H}_2\text{O}_{\text{m},5200}$  peak vary significantly. Variation within the  $\text{H}_2\text{O}_{\text{m},5200}$  peak concentrations approach 1.00 wt% for D1010 and span over 2.00 wt.% for CN92C-OL2. Some of the variability is captured within the uncertainty of the peak fits, but the reproducibility of  $\text{H}_2\text{O}_{\text{m},1635}$  concentrations allows for greater confidence to be placed in the peak fits. The variability in the data collected from the near-infrared region can be attributed to the small amplitude of the peaks. The stability of the mid-infrared  $\text{H}_2\text{O}_{\text{m},1635}$  peak is due to its greater amplitude with respect to the baseline, as a more significant peak.

Unsaturated glass analyses further allow for analysis of the quality of near-infrared peaks. Reconstructing  $\text{H}_2\text{O}_{\text{t}}$  from the combination of either  $\text{H}_2\text{O}_{\text{m}}$  and the  $\text{OH}_{4500}^-$  concentrations allows for comparison with concentrations determined from the  $\text{H}_2\text{O}_{\text{t},3550}$  peak. This comparison reveals that using the  $\text{H}_2\text{O}_{\text{m},1635}$  peak results in higher concordance correlation coefficients (CCC), a measure of the agreement between two variables [Lin 1989], as well as lower root-mean-square errors (unit-dependent), lower relative root-mean-square errors (unitless), and higher coefficients of determination (Figure 10C, Figure 10D). The concordance correlation coefficient serves as a more comprehensive measure by capturing both the correlation and agreement between the reconstructed concentrations and the reference. While the coefficient of determination provides information on the proportion of variance in the data explained by the prediction model and the root-mean-square error provides insight into the precision of predictions, neither gives a complete picture of how well predictions agree with actual values. The concordance correlation coefficient integrates both these aspects, ensuring that not only are our predictions closely related to actual values (high correlation) but also that they closely match the actual values (high agreement). Hence, in assessing the accuracy of reconstruction, a higher concordance correlation coefficient serves as a more robust indicator of efficacy [Lin 1989]. Reconstructing  $\text{OH}^-$  from the subtraction of either  $\text{H}_2\text{O}_{\text{m}}$  peak from the  $\text{H}_2\text{O}_{\text{t},3550}$  peak and comparing those concentrations against the  $\text{OH}_{4500}^-$  peak similarly shows that the  $\text{H}_2\text{O}_{\text{m},1635}$  peak yields higher concordance correlation coefficients, lower root-mean-square errors and relative root-mean-square errors, and higher coefficients of determination (Figure 10E, Figure 10F). We recommend use of the  $\text{H}_2\text{O}_{\text{m},1635}$  peak over the  $\text{H}_2\text{O}_{\text{m},5200}$  peak when calculating  $\text{H}_2\text{O}_{\text{t}}$  for saturated samples, due to the better accuracy, precision, and reproducibility of the  $\text{H}_2\text{O}_{\text{m},1635}$  peak across sessions.

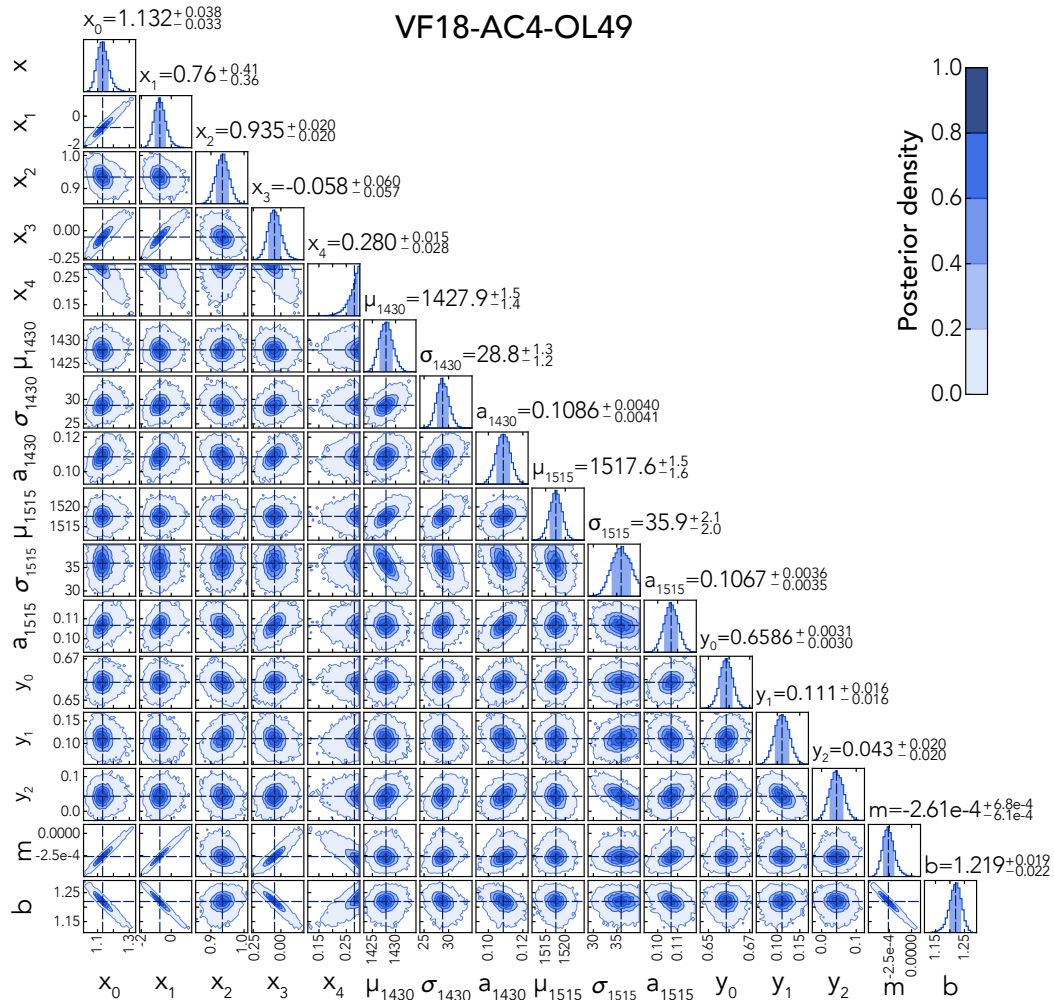


Figure 8: Posterior probability density distribution for the 16 coefficients or parameters of Equation 10 for olivine-hosted melt inclusion VF18-AC4-OL49, fit with PyIRoGlass over  $10^6$  samples. See Table 2 for additional information about the coefficients and parameters.  $x_n$  best-fit coefficients generating the baseline scale the  $\underline{\text{Baseline}}$  and  $\underline{\text{Baseline}}_{\text{PC1-4}}$  vectors.  $y_n$  best-fit coefficients for fitting the  $\text{H}_2\text{O}_{m,1635}$  peak scale the  $\underline{\text{H}_2\text{O}_{m,1635}}$  and  $\underline{\text{H}_2\text{O}_{m,1635\text{PC1-2}}}$  vectors. Parameters for fitting the  $\text{CO}_3^{2-}$  doublet include the subscripted parameters  $a$ ,  $\sigma$ , and  $\mu$ ; parameters for fitting the linear shift include  $m$  and  $b$ . Several parameters covary, demonstrating the importance of assessing underlying covariance structures to properly account for uncertainty within this ensemble solution.

### 3.5 Synthetic and Natural Glasses: A Test Dataset

Two questions remain regarding the performance of PyIRoGlass, as we test the performance of the MCMC technique with Bayesian inference. First, are we reproducing the ‘true’ devolatilized baseline? We answer this question by comparing PyIRoGlass baselines to a set of experimentally devolatilized (‘true’) baselines (Table 3, Section 3.5.1). Second, are we reproducing absolute concentrations? We answer this question by comparing PyIRoGlass results with published values for an array of interlaboratory standards (Table 4, Section 3.5.2).

#### 3.5.1 PyIRoGlass Performance on Synthetic Glasses with Devolatilized Baselines

We assess the performance of PyIRoGlass baselines against the ‘true’ devolatilized baseline by turning to a test dataset

consisting of 28 synthetic glasses of basaltic, andesitic, and basaltic compositions from Lee et al. [2024] and Moussallam et al. [2024]. These glasses range in  $\text{H}_2\text{O}$  from 0.2 to 5.85 wt.% and in  $\text{CO}_2$  from 0.09 to 1.60 wt.%. For each of these glasses, a corresponding chemistry- and matrix-matched devolatilized glass was available (Table 3). The volatilized and corresponding devolatilized glasses are synthesized from the same starting materials and are compositionally near-identical (agreement within 10%, with a mean deviation of 4%). All experimental details can be found in Lee et al. [2024] and Moussallam et al. [2024].

For each of the 28 volatilized glasses, we apply PyIRoGlass to the transmission FTIR spectrum to determine the best-fit baseline and peak amplitudes. We then compare these PyIRoGlass peak amplitudes with those determined from a simple

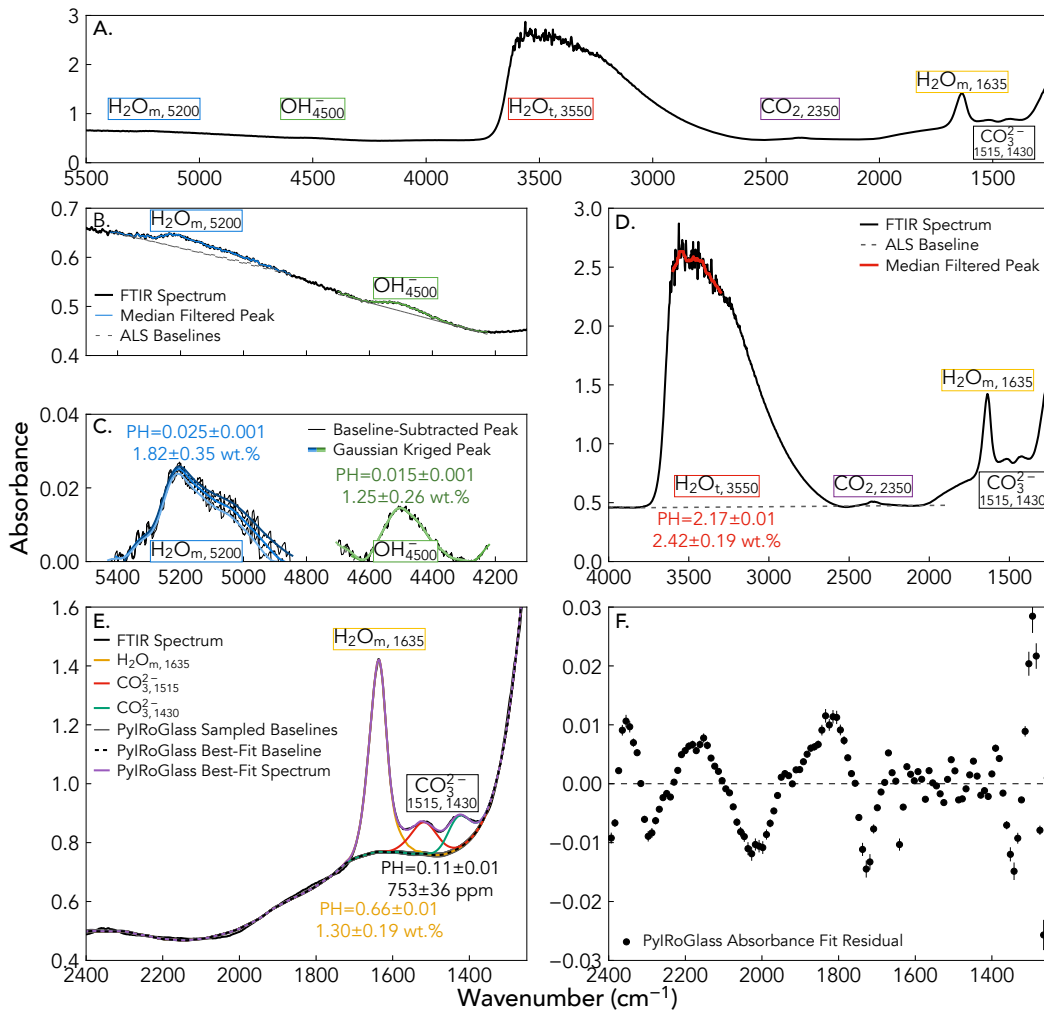


Figure 9: PyIRoGlass baseline and peak fits for the transmission FTIR spectrum of olivine-hosted melt inclusion VF18-AC4-OL49. OL49 has a thickness of  $91 \pm 3 \mu\text{m}$ . Uncertainties in peak amplitudes are small within the ensemble solution of PyIRoGlass's fitting framework; most uncertainties in volatile concentrations are introduced by uncertainties in molar absorptivity and thickness. A. Transmission FTIR spectrum through the near-IR and mid-IR region. OL49's ragged  $\text{H}_2\text{O}_{\text{t},3550}$  peak indicates saturation, prompting the determination of  $\text{H}_2\text{O}_{\text{t}}$  from  $\text{H}_2\text{O}_{\text{m},1635} + \text{OH}^-_{4500}$  (see Section 3.4). B.  $\text{H}_2\text{O}_{\text{m},5200}$  and  $\text{OH}^-_{4500}$  baselines in the near-IR region. Three ALS-derived baselines are generated by sampling slightly different regions around each peak, to assess uncertainty in peak location. C.  $\text{H}_2\text{O}_{\text{m},5200}$  and  $\text{OH}^-_{4500}$  baseline-subtracted peaks, with kriging interpolation. Mean peak amplitudes with uncertainties are determined from the three baseline-subtracted peaks. D. Saturated  $\text{H}_2\text{O}_{\text{t},3550}$  peak. Three ALS-derived baselines are generated by sampling slightly different regions around each peak, although this saturated peak is not used. E. Best-fit baselines and peaks for the  $\text{H}_2\text{O}_{\text{m},1635}$  peak and  $\text{CO}_3^{2-}$  doublet, with baseline fits over  $10^6$  samples.  $\text{H}_2\text{O}_{\text{t}}$  equals  $2.55 \pm 0.16 \text{ wt.}\%$ , combining  $\text{H}_2\text{O}_{\text{m},1635} + \text{OH}^-_{4500}$ . F. Absorbance residual between the best-fit PyIRoGlass spectrum and the measured spectrum. Residuals lie between  $\pm 0.01$  in the wavenumber region beneath the  $\text{H}_2\text{O}_{\text{m},1635}$  peak and  $\text{CO}_3^{2-}$  doublet.

least squares baseline subtraction of the devolatilized glass spectrum from the volatilized glass spectrum. Replicate analyses of these 28 synthetic volatilized glasses, which have variable thicknesses, form a dataset of 148 spectra. All spectra of volatilized glasses, along with their devolatilized counterparts, are available on GitHub and Zenodo.

$\text{CO}_{3,1515}^{2-}$  and  $\text{CO}_{3,1430}^{2-}$  doublet peak amplitudes derived from PyIRoGlass and from devolatilized baselines show strong agreement through  $50 \mu\text{m}$  normalized absorbances of 2.25, within 10% uncertainty bounds (Figure 11A, Figure 11B). Agreement between the samples is demonstrated by the high concordance correlation coefficient, low root-mean-square er-

rors and relative root-mean-square errors, high coefficients of determination, slopes exceeding 0.91, and intercepts approximating 0. Stronger agreement is found in the  $\text{CO}_{3,1430}^{2-}$  peak amplitudes, indicated by the ratio between peak amplitudes from PyIRoGlass and the devolatilized baseline or  $\frac{P}{D}$  (Figure 11C, Figure 11D). Scatter (and potentially noise) is evident where peak amplitudes are below 0.50, with  $\frac{P}{D}$  ranging from 0.86-1.04. Distinct mean peak amplitude ratios ( $\frac{P}{D}$ ) of 0.934 for the  $\text{CO}_{3,1515}^{2-}$  peak and of 0.950 for the  $\text{CO}_{3,1430}^{2-}$  emerge. The similarity between baseline fits—and consequently peak amplitudes—and strength of statistical reproduction suggest



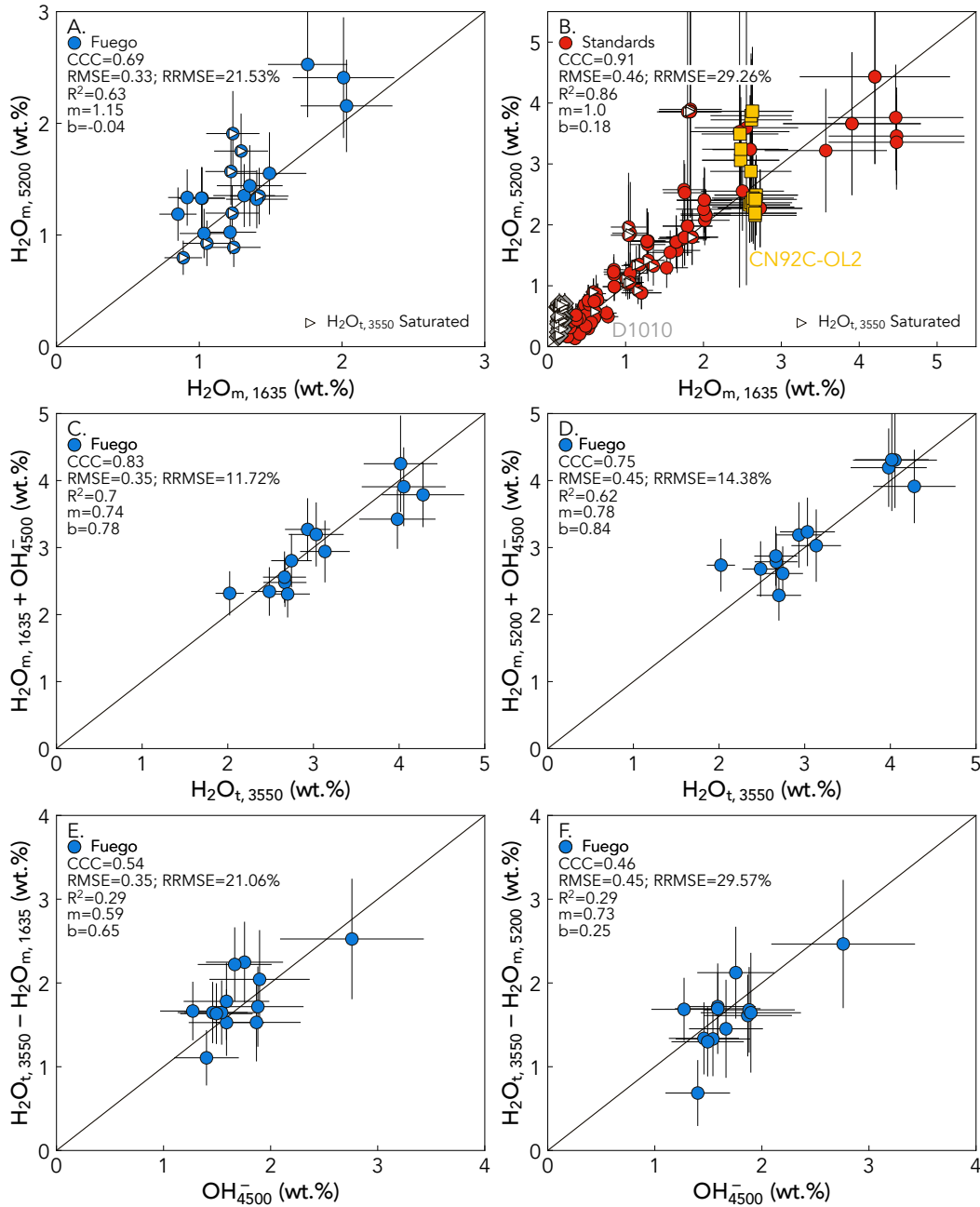


Figure 10: Comparison of the  $H_2O_{m,1635}$  and  $H_2O_{m,5200}$  peaks.  $H_2O_{t,3550}$ -saturated glasses are marked with a white triangle. A.  $H_2O_{m,1635}$  and  $H_2O_{m,5200}$  concentrations in Volcán de Fuego melt inclusions. Most melt inclusion analyses have higher concentrations of  $H_2O_{m,5200}$  than  $H_2O_{m,1635}$ . B.  $H_2O_{m,1635}$  and  $H_2O_{m,5200}$  concentrations in the internal check standards given in Section 3.2. Most analyses have higher concentrations of  $H_2O_{m,5200}$  than  $H_2O_{m,1635}$ . Significant variability is observed for replicate analyses of internal standards D1010 (grey diamonds) and CN92C-OL2 (yellow squares), forming expansive vertical bands. Note that sample D1010 is saturated in  $H_2O_{t,3550}$  despite its low  $H_2O_{m,1635}$ , due to its thickness of 231  $\mu\text{m}$  and concentration of  $0.93 \pm 0.10$  wt.%  $H_2O_t$ . C.  $H_2O_t$  from  $H_2O_{m,1635} + OH_{4500}^-$ . D.  $H_2O_t$  from  $H_2O_{m,5200} + OH_{4500}^-$ . E.  $OH_{4500}^-$  from  $H_2O_{t,3550} - H_2O_{m,1635}$ . F.  $OH_{4500}^-$  from  $H_2O_{t,3550} - H_2O_{m,5200}$ .

that PyIRoGlass properly derives and constructs baselines to fit basaltic to andesitic glasses. There are some differences between peak amplitudes derived from PyIRoGlass and devolatilized baselines, notably a 5.0 - 6.5% offset in the two methods (Figure 11C, Figure 11D). A closer examination of the peaks and baselines generated for the test dataset can shed light on the causes of this offset (Figure 12).

Baselines from PyIRoGlass and devolatilized glasses can be nearly identical (Figure 12A, Figure 12B), but also reveal some meaningful differences (Figure 12C, Figure 12D). Spectra CI-Ref-6 and CI-Ref-10 (Figure 12A, Figure 12B) demonstrate the success of PyIRoGlass in reconstructing the devolatilized baseline and in fitting the  $H_2O_{m,1635}$  peak and  $CO_3^{2-}$  doublet. PyIRoGlass considers the convolution of the  $H_2O_{m,1635}$

1025

1030

1035

peak with the  $\text{CO}_2^-_{3,1515}$  peak, resulting in the plotted Gaussian  $\text{CO}_2^-_{3,1515}$  not reaching the top of the spectrum. On the other hand, the absorbances determined by simple least squares subtraction of the devolatilized baselines do not account for peak convolution and the contribution of the  $\text{H}_2\text{O}_{\text{m},1635}$  peak. This effect is apparent in the slightly lower  $\frac{P}{D}$  for  $\text{CO}_2^-_{3,1515}$  compared to  $\text{CO}_2^-_{3,1430}$  (Figure 11C, Figure 11D). The pervasive offset of  $\sim 6\%$  (the uniformly lower  $\frac{P}{D}$  ratio for both  $\text{CO}_2^-$  peaks) requires a different explanation that involves a mismatch in the baseline. Spectra CI-Ref-Bas-9 and CI-Ref-27 (Figure 12C, Figure 12D) both show greater scooping in the devolatilized baselines than predicted by PyIRoGlass. Such scooping would lead to greater  $\text{CO}_2^-$  absorbances for both peaks in the devolatilized baseline approach. While this could be a shortcoming of the baseline dataset input (spectra with volatiles below detection) into PyIRoGlass, it could also be an artifact of the experimental procedure, whereby experimental conditions with no control on oxygen fugacity may have altered the devolatilized glass and therefore the baseline (see Section 3.7). Evidence for this lies in the mismatch between the measured Spectrum CI-Ref-27, and the experimentally devolatilized baseline (Figure 12D), showing a lack of overlap in the region between 1800 and 2300  $\text{cm}^{-1}$ . This suggests alterations during the experimental heating that affected the shape of the baseline. The PyIRoGlass ensemble solution, which accounts for a multiplicity of baseline shapes, better matches the measured spectrum for CI-Ref-27. Nonetheless, agreement between baselines from PyIRoGlass and experimental devolatilization within 6% is still highly satisfactory. And PyIRoGlass can continue to be improved by incorporating baselines from more spectra with volatiles below detection, from a wider array of compositions.

### 3.5.2 PyIRoGlass Performance on Published Test Dataset

Next, we compare PyIRoGlass  $\text{H}_2\text{O}$  and  $\text{CO}_2$  concentrations calculated from a self-consistent set of FTIR measurements (all at LDEO on the same FTIR, see Table 4 and Supplement for information on analytical conditions). These include previous studies of volatiles in natural back-arc basin glasses measured by FTIR and SIMS [Pearce et al. 1994; Newman et al. 2000; Rasmussen 2019; Barth 2021; Lytle et al. 2023] or synthetic glasses by FTIR, SIMS, KFT, EA, ERDA, or NRA [Shishkina et al. 2010; Helo et al. 2011; Fiege et al. 2015; Brounce et al. 2021; Moussallam et al. 2024]. Natural glasses include back-arc basin basalts D1010, ALV1833-11, WOK5-4, and ALV1846-9 analyzed with FTIR by Newman et al. [2000]; CD33-12-2-2 and CD33-22-1-1 analyzed with SIMS by Lytle et al. [2023]; ETFSR-OL8 analyzed with SIMS by Barth [2021]. Back-arc basin glasses analyzed with FTIR utilize baselines from a least squares fitting technique, using a single reference baseline and peak components, described by Newman et al. [2000]. Synthetic glasses include the high-Mg basaltic glasses ABWCl-F0x and ABWB-0x analyzed with KFT for  $\text{H}_2\text{O}$  by Fiege et al. [2015]; boninites BF73, BF76, and BF77 analyzed with KFT for  $\text{H}_2\text{O}$  and elemental analyzer (EA) for  $\text{CO}_2$  by Brounce et al. [2021]; basalts M35 and M43 analyzed with KFT for  $\text{H}_2\text{O}$  and FTIR for  $\text{CO}_2$  by Shishkina et al. [2010]; synthetic basalts of

the ND70-series analyzed with SIMS and ERDA for  $\text{H}_2\text{O}$  and NRA for  $\text{CO}_2$  by Moussallam et al. [2024]; synthetic basalt NS-1 analyzed with FTIR for  $\text{H}_2\text{O}$  and  $\text{CO}_2$  by Helo et al. [2011]; synthetic basaltic andesite INSOL-MX1-BA4 analyzed with FTIR for  $\text{H}_2\text{O}$  and  $\text{CO}_2$  by Moussallam et al. [2024]. Utilizing PyIRoGlass to determine volatile concentrations from the re-analyzed transmission spectra of samples, with published concentrations from alternate analytical techniques, allows for the validation of concentration measurements. Glasses analyzed with SIMS, KFT, EA, ERDA, and NRA allow for comparison against more independent analytical techniques, although many calibrations rely on standards analyzed by FTIR.

Application of PyIRoGlass to the test dataset shows that  $\text{H}_2\text{O}$  determined by FTIR primarily agree with published values up to concentrations of approximately 6.0 wt.%, even when the  $\text{H}_2\text{O}_{\text{t},3550}$  peak is saturated and we calculate  $\text{H}_2\text{O}_{\text{t}}$  from the  $\text{H}_2\text{O}_{\text{m},1635}$  and  $\text{OH}^-_{4500}$  peaks (Figure 13A). Agreement between concentrations is demonstrated by the high concordance correlation coefficient, low root-mean-square error and relative root-mean-square error of  $\sim 10\%$ , high coefficient of determination, slope nearing 1, and intercept nearing 0. The calculated  $\text{H}_2\text{O}_{\text{t}}$  from glasses synthesized by Fiege et al. [2015] are well represented by the combined  $\text{H}_2\text{O}_{\text{m},1635}$  and  $\text{OH}^-_{4500}$  concentrations despite saturation, discussed in Section 3.4. Offsets observed in back-arc basin glasses D1010, ALV1833-11, WOK5-4, and ALV1846-9 can likely be attributed to differences in fitting methodologies, fitting regions, and potential heterogeneity in analyzed glass wafers. Inversion and published molar absorptivities ( $63 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}$ ) agree within  $1 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}$ . The remaining samples within the test dataset agree within the uncertainties of analysis at concentrations below 6.0 wt.%  $\text{H}_2\text{O}$ , across FTIR, SIMS, KFT, and ERDA.

PyIRoGlass demonstrates strong agreement in  $\text{CO}_2$  determined by FTIR, SIMS, EA, and NRA through concentrations of 1.6 wt.% for back-arc basin and synthetic glasses (Figure 13B). The low  $\text{H}_2\text{O}$  and low  $\text{CO}_2$  back-arc basin basalts, along with the synthetic boninites (BF73, BF76, BF77) and synthetic basalts (NS-1, ND70-series), provide coverage over a significant range of volatile concentrations. For glasses with published concentrations using FTIR, we use the molar absorptivities provided in each respective study to calculate concentrations. This is for the sake of consistency, to highlight the baseline fitting in PyIRoGlass, our primary objective. Overall, strong agreement in  $\text{CO}_2$  concentrations between PyIRoGlass and the other published results (Figure 13B) is demonstrated by the high concordance correlation coefficient, low root-mean-square error and relative root-mean-square error of  $\sim 6\%$ , high coefficient of determination, slope nearing 1, and intercept nearing 0. If we used the compositionally-dependent molar absorptivities in Figure 5, results would be  $\sim 30\%$  lower for the Brounce et al. [2021] BF glasses and  $\sim 12\%$  higher for the Helo et al. [2011] NS-1 glass. Clearly, more work resolving the compositional effects on the molar absorptivity of the  $\text{CO}_2$  peaks is welcome.

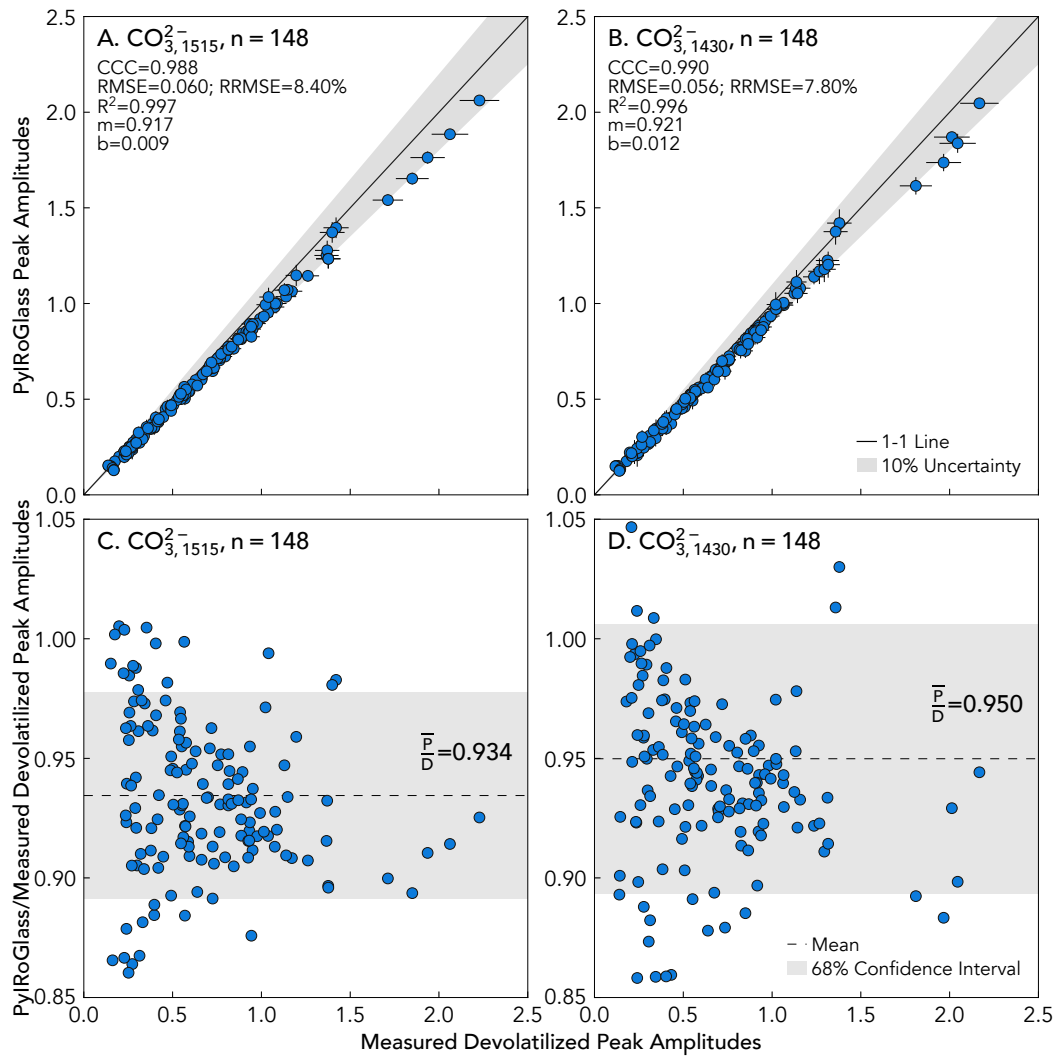


Figure 11: Peak amplitudes between PylRoGlass and devolatilized baselines for synthesized basalt, andesite, and basanite glasses (Table 3). Peak amplitudes are all normalized to a thickness of 50  $\mu\text{m}$  to demonstrate the significant range of concentrations. 1 sigma peak amplitude uncertainties from PylRoGlass are plotted, along with 5% uncertainty imposed on peak amplitudes from the devolatilized method. A. Peak amplitudes for  $\text{CO}_{3,1515}^{2-}$ . B. Peak amplitudes for  $\text{CO}_{3,1430}^{2-}$ . PylRoGlass peak amplitudes mostly fall within 10% uncertainty of the devolatilized peak amplitudes, with  $\text{CO}_{3,1430}^{2-}$  showing stronger agreement. C. Peak amplitude ratios generated by the two methods (PylRoGlass/Devolatilized, or  $\frac{P}{D}$ ) for  $\text{CO}_{3,1515}^{2-}$ , with a mean ratio of 0.934. D. Peak amplitude ratios for  $\text{CO}_{3,1430}^{2-}$ , with a mean ratio of 0.950. Peak amplitude ratios at lower absorbances incorporate more significant noise.

### 3.6 Detection Limit for Volatile Species

1150 Previous determinations of FTIR detection limits for glasses  
 have primarily relied on either estimations of operational limits  
 (converted to concentration) for recognizable peaks [Fine and  
 Stolper 1985; 1986; Newman et al. 1986; Dixon and  
 Stolper 1995; Newman et al. 2000] or utilized the ‘practical’  
 1155 quantification of the lowest concentrations of an analyte in  
 a given sample [Mercier et al. 2010; Lowenstern and Pitcher  
 2013]. The detection limit, or LOD, is defined as the minimum  
 concentration of an analyte that is distinguishable from a  
 background or blank, and is quantified by calculating three  
 1160 times the standard deviation of the background signal [Analytical  
 Methods Committee 1987]. Quantification of the detection

limit occurs within the signal domain (absorbance for FTIR)  
 and is reported within the concentration domain, with the  
 Beer-Lambert Law serving as the calibration function [Delgado  
 2022]. Concentrations and thickness are correlated by the  
 Beer-Lambert Law. Thicker samples yield stronger signals  
 in absorbance, but risk saturation when this signal is too  
 strong and insufficient light is transmitted to the detector.  
 Achieving the balance between signal intensity and noise is  
 critical to high-quality analyses with low detection limits  
 1170 [Newman et al. 1986].

We assess the detection limits for each volatile peak within  
 the dataset of synthetic and natural glasses (Section 3.5),  
 where concentrations are well determined. The baseline is  
 considered as the background, as it captures the spectrum of a  
 1175

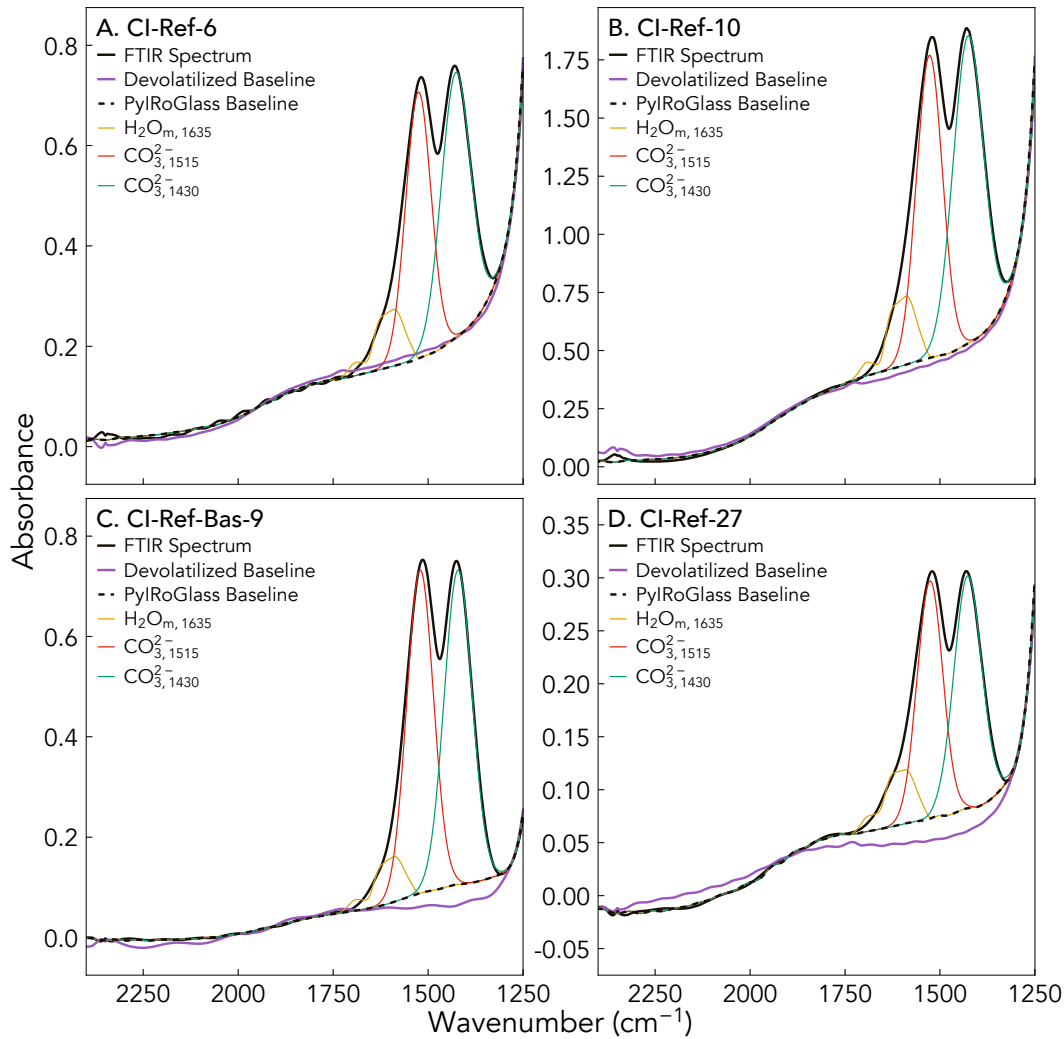


Figure 12: Comparison of PyIRoGlass and devolatilized baselines for four exemplar spectra. Spectra are presented as analyzed, without thickness normalization. A. CI-Ref-6 with strong baseline agreement, B. CI-Ref-10 with strong baseline agreement. C. CI-Ref-Bas-9 with the devolatilized baseline accommodating greater scooping beneath  $\text{CO}_3^{2-}$  peaks. D. CI-Ref-27 with the devolatilized baseline accommodating greater scooping beneath  $\text{CO}_3^{2-}$  peaks, but with divergence of baselines past  $1800 \text{ cm}^{-1}$ .

ple without volatiles. To determine the variability in the background signal, we calculate three times the standard deviation of the PyIRoGlass sampled baselines. For the  $10^6$  sampled baselines underlying the  $\text{H}_2\text{O}_{\text{m},1635}$  and  $\text{CO}_3^{2-}$  peaks, we first remove burn-in samples and then utilize the best-fit peak locations from PyIRoGlass to calculate the standard deviation in the sampled baselines (see Figure 9E). This captures the background variability within the baseline. For the three repeat baselines underlying the  $\text{H}_2\text{O}_{\text{m},5200}$ ,  $\text{OH}_{4500}^-$ , and  $\text{H}_2\text{O}_{\text{t},3550}$  peaks, we directly calculate the standard deviation in the background with the nominal peak locations. We consider only samples with signal-to-noise ratios exceeding 4 for the  $\text{H}_2\text{O}_{\text{m},5200}$  and  $\text{OH}_{4500}^-$  peaks, and unsaturated samples for the  $\text{H}_2\text{O}_{\text{t},3550}$  peak. Three times these standard deviations in the baseline absorbances were converted to concentrations with the Beer-Lambert Law, incorporating the  $\epsilon$ ,  $l$ , and  $\rho$  values obtained from PyIRoGlass as scaling factors.

Detection limits directly correlate with measured sample thickness, and this relationship can be defined with a recip-

rocal function (Figure 14). The shape of the reciprocal function is rooted in the presence of thickness in the denominator of the Beer-Lambert Law, with the detection limit increasing rapidly as thickness approaches zero. Despite the inextricable nature of thickness within the concentration space, this practice provides a useful quantification of the detection limit and further demonstrates the differential background and detector sensitivity across the analyzed spectral region. The reciprocal function holds the form:

$$LOD = \frac{a}{l} + b, \quad (12)$$

where  $l$  is the wafer thickness, and  $a$  and  $b$  are fit with least squares optimization from the scikit-learn package [Pedregosa et al. 2011].

Detection limits for the  $\text{H}_2\text{O}_{\text{m},1635}$  and  $\text{CO}_3^{2-}$  peaks, with PyIRoGlass MCMC sampled baselines, are well fit by the reciprocal function (Figure 14A, Figure 14B, Figure 14C). The reciprocal functions fitting these peaks are associated with high

Table 3: Synthetic volatilized glasses with devolatilized baselines, from Lee et al. [2024] and Moussallam et al. [2024], in the test dataset. Experiments performed by piston cylinder and analyses performed with the Thermo Scientific Nicolet iN10 MX Fourier Transform Infrared Spectrometer, both at the Lamont-Doherty Earth Observatory.  $1\sigma$  uncertainties propagate analytical, fitting, and replicate analysis uncertainties. Peak amplitudes are normalized to  $50\ \mu\text{m}$ .

Sample	Composition	n	CO <sub>2,1515</sub> Devolatilized Peak Height	PylRoGlass CO <sub>2,1515</sub> Peak Height	PylRoGlass $\sigma$ CO <sub>2,1515</sub> Peak Height	CO <sub>2,1430</sub> Devolatilized Peak Height	PylRoGlass CO <sub>2,1430</sub> Peak Height	PylRoGlass $\sigma$ CO <sub>2,1515</sub> Peak Height	PylRoGlass H <sub>2</sub> O (wt.%)	$\sigma$ PylRoGlass H <sub>2</sub> O (wt.%)	PylRoGlass CO <sub>2</sub> (ppm)	$\sigma$ PylRoGlass CO <sub>2</sub> (ppm)
CI-LMT-BA3	Synthetic Basaltic Andesite	1	1.040	1.034	0.012	1.021	0.995	0.016	0.43	0.11	10278	1717
CI-LMT-BA4	Synthetic Basaltic Andesite	1	1.367	1.251	0.006	1.312	1.225	0.007	0.33	0.04	12553	845
CI-LMT-BA17	Synthetic Basaltic Andesite	2	2.145	1.973	0.005	2.090	1.958	0.006	0.23	0.05	19023	1778
CI-Ref-4	Synthetic MORB	2	1.007	0.924	0.003	0.992	0.938	0.003	1.11	0.11	8876	542
CI-Ref-6	Synthetic MORB	8	0.553	0.514	0.003	0.544	0.514	0.004	1.02	0.10	4880	294
CI-Ref-8	Synthetic MORB	5	0.930	0.858	0.004	0.913	0.862	0.005	0.88	0.10	8924	640
CI-Ref-9	Synthetic MORB	2	0.909	0.836	0.002	0.883	0.832	0.002	1.61	0.13	8862	422
CI-Ref-10	Synthetic MORB	8	0.626	0.574	0.003	0.635	0.597	0.003	0.80	0.07	5439	866
CI-Ref-11	Synthetic MORB	4	0.891	0.815	0.007	0.872	0.813	0.010	1.27	0.49	7688	2295
CI-Ref-14	Synthetic MORB	2	0.349	0.318	0.007	0.330	0.307	0.009	1.07	0.15	2942	468
CI-Ref-15	Synthetic MORB	3	0.275	0.250	0.013	0.247	0.232	0.016	1.00	1.11	2315	542
CI-Ref-18	Synthetic MORB	5	0.303	0.286	0.006	0.293	0.280	0.008	1.01	0.14	2686	378
CI-Ref-20	Synthetic MORB	5	0.310	0.296	0.005	0.299	0.288	0.007	0.78	0.10	2755	380
CI-Ref-23	Synthetic MORB	4	0.245	0.228	0.003	0.240	0.227	0.004	1.01	0.09	2178	180
CI-Ref-25	Synthetic MORB	10	0.993	0.916	0.004	0.982	0.925	0.005	0.86	0.19	7968	1947
CI-Ref-27	Synthetic MORB	6	0.581	0.546	0.006	0.570	0.543	0.008	1.14	0.19	5163	818
CI-Ref-28	Synthetic MORB	6	0.950	0.883	0.006	0.939	0.884	0.007	1.34	0.16	8433	1084
CI-Ref-bas-3	Synthetic Basanite	7	0.682	0.643	0.007	0.675	0.626	0.009	1.51	0.25	6784	952
CI-Ref-bas-5	Synthetic Basanite	3	0.222	0.222	0.006	0.225	0.218	0.007	1.62	0.19	2353	639
CI-Ref-bas-6	Synthetic Basanite	3	0.937	0.861	0.007	0.930	0.849	0.009	1.69	0.23	9368	1497
CI-Ref-bas-7	Synthetic Basanite	9	0.440	0.412	0.009	0.433	0.404	0.011	1.38	0.23	4397	1410
CI-Ref-bas-8	Synthetic Basanite	8	0.483	0.456	0.007	0.486	0.450	0.009	1.29	0.21	4719	1235
CI-Ref-bas-9	Synthetic Basanite	14	0.651	0.609	0.007	0.655	0.599	0.009	1.30	0.56	7429	4277
ND70-2-01	Synthetic Basalt	6	0.155	0.143	0.003	0.133	0.140	0.003	2.12	0.34	1304	122
ND70-3-01	Synthetic Basalt	7	0.259	0.248	0.005	0.229	0.237	0.005	3.43	0.97	2263	409
ND70-4-02	Synthetic Basalt	8	0.474	0.446	0.003	0.440	0.427	0.004	3.86	0.89	4161	631
ND70-5-02	Synthetic Basalt	6	1.356	1.277	0.013	1.292	1.243	0.017	5.16	0.59	12057	1221
ND70-6-02	Synthetic Basalt	3	1.833	1.652	0.008	1.940	1.730	0.012	5.85	0.96	16018	1864

Table 4: Back-arc basin glasses (BAB), melt inclusions (MI), and synthetic glasses forming the test dataset, with stated sources – both in terms of publication and analysis location. All glasses were distributed to and re-analyzed by FTIR at Lamont-Doherty Earth Observatory (LDEO), with the exception of the ALV, WOK, and CD series glasses re-analyzed by FTIR at the National Museum of Natural History, Smithsonian Institution. Published analytical technique and locations – FTIR at California Institute of Technology (Caltech) fits baselines with the Newman et al. [2000] least squares fitting technique with a single baseline and H<sub>2</sub>O<sub>m,1635</sub> peak component; FTIR at Institut für Mineralogie, Leibniz Universität Hannover (Hannover) fits tangential baselines; FTIR at American Museum of Natural History (AMNH) and LDEO fits a devolatilized baseline; SIMS analyses performed at Carnegie Institution for Science (CIS) and Centre de Recherches Pétrographiques et Géochimiques, Université de Lorraine (Nancy); ERDA and NRA performed at the Laboratoire d'Etude des Eléments Légers (LEEL) joint CEA-CNRS laboratory at Université Paris-Saclay. Volatile concentrations and uncertainties are presented as provided within the reference within the published concentration column.  $1\sigma$  uncertainties propagate analytical, fitting, and replicate analysis uncertainties. 10% uncertainty is imposed when uncertainties are not reported, or where published uncertainties are unrealistic given inherent uncertainties (thickness and molar absorptivity in FTIR). - indicates that there is no published measurement or uncertainty, and bdl indicates that concentrations were below detection limits.

Sample	Reference	Composition	Published Analytical Technique	n	Published H <sub>2</sub> O (wt.%)	Published $\sigma$ H <sub>2</sub> O (wt.%)	PylRoGlass H <sub>2</sub> O (wt.%)	PylRoGlass $\sigma$ H <sub>2</sub> O (wt.%)	Published CO <sub>2</sub> (ppm)	Published $\sigma$ CO <sub>2</sub> (ppm)	PylRoGlass CO <sub>2</sub> (ppm)	PylRoGlass $\sigma$ CO <sub>2</sub> (ppm)	PylRoGlass CO <sub>2</sub> (ppm) published $\pm$	PylRoGlass $\sigma$ CO <sub>2</sub> (ppm) with published $\pm$
ABWCI-F0x	Fiege et al. [2015]	Synthetic High-Mg Basalt	FTIR-Hannover	3	2.97	0.29	3.19	0.48	-	-	435	66	-	-
ABWB-0x	Fiege et al. [2015]	Synthetic High-Mg Basalt	RFT-Hannover	4	4.40	0.40	3.88	0.49	-	-	1400	47	-	-
ALV1833-11	Neuman et al. [2000]	BAB-Mariana Trough	FTIR-Caltech	3	1.20	0.12	1.02	0.08	102	10	35	9	30	8
21ALV1846-9	Neuman et al. [2000]	BAB-Mariana Trough	FTIR-Caltech	3	1.89	0.19	1.42	0.12	bdl	bdl	bdl	bdl	bdl	bdl
23WV05-4	Neuman et al. [2000]	BAB-Mariana Trough	FTIR-Caltech	3	1.60	0.16	1.01	0.08	64	6	21	6	18	5
BF73	Brounce et al. [2021]	Synthetic Boninite	RFT/EA/FTIR-Hannover	3	0.72	0.07	0.82	0.06	2995	190	2417	77	3042	97
BF76	Brounce et al. [2021]	Synthetic Boninite	RFT/EA/FTIR-Hannover	3	0.67	0.07	0.75	0.06	2336	127	1843	78	2319	98
BF77	Brounce et al. [2021]	Synthetic Boninite	RFT/EA/FTIR-Hannover	3	0.70	0.07	0.86	0.08	1030	27	708	57	891	72
CD33-12-2-2	Pearce et al. [1994], Lyle et al. [2023]	BAB-Lau Basin	SIMS-CIS	3	0.27	0.03	0.27	0.02	170	17	131	14	-	-
CD33-22-1-1	Pearce et al. [1994], Lyle et al. [2023]	BAB-Lau Basin	SIMS-CIS	3	0.49	0.05	0.53	0.05	109	11	67	16	-	-
D1010	Neuman et al. [2000]	BAB-Mariana Trough	FTIR-Caltech	34	1.13	0.07	0.93	0.15	139	14	179	41	149	34
ETFSR-OL8	Barth [2021]	MI-Ema	SIMS-Nancy	3	4.16	0.42	3.85	0.43	-	-	5311	344	-	-
M35	Shishikina et al. [2010]	Synthetic Basalt	RFT/FTIR-Hannover	3	4.20	0.12	4.10	0.51	1019	81	975	106	1000	109
M43	Shishikina et al. [2010]	Synthetic Basalt	RFT/FTIR-Hannover	3	2.62	0.11	2.52	0.32	3172	265	2735	253	2857	264
ND70-2-01	Moussallam et al. [2024]	Synthetic Basalt	ERDA/NRA-CEA-CNRS	6	2.53	0.24	2.12	0.34	1837	35	1304	122	1304	122
ND70-3-01	Moussallam et al. [2024]	Synthetic Basalt	ERDA/NRA-CEA-CNRS	7	3.13	0.30	3.43	0.97	2689	54	2263	409	2263	409
ND70-4-02	Moussallam et al. [2024]	Synthetic Basalt	ERDA/NRA-CEA-CNRS	8	3.68	0.35	3.86	0.89	4122	65	4161	631	4161	631
ND70-5-02	Moussallam et al. [2024]	Synthetic Basalt	ERDA/NRA-CEA-CNRS	6	5.34	0.51	5.16	0.60	13662	105	13057	1221	12057	1221
ND70-6-02	Moussallam et al. [2024]	Synthetic Basalt	ERDA/NRA-CEA-CNRS	3	6.26	0.59	5.85	0.96	16847	120	16018	1864	16018	1864
NS-1	Helo et al. [2011]	Synthetic Basalt	FTIR-AMNH	3	0.37	0.04	0.35	0.03	3154	158	4273	173	3546	144
INSOL-MX1-BA4	Moussallam et al. [2024]	Synthetic Basaltic Andesite	FTIR-LDEO	3	0.15	0.01	0.15	0.01	8207	377	8044	367	8044	367

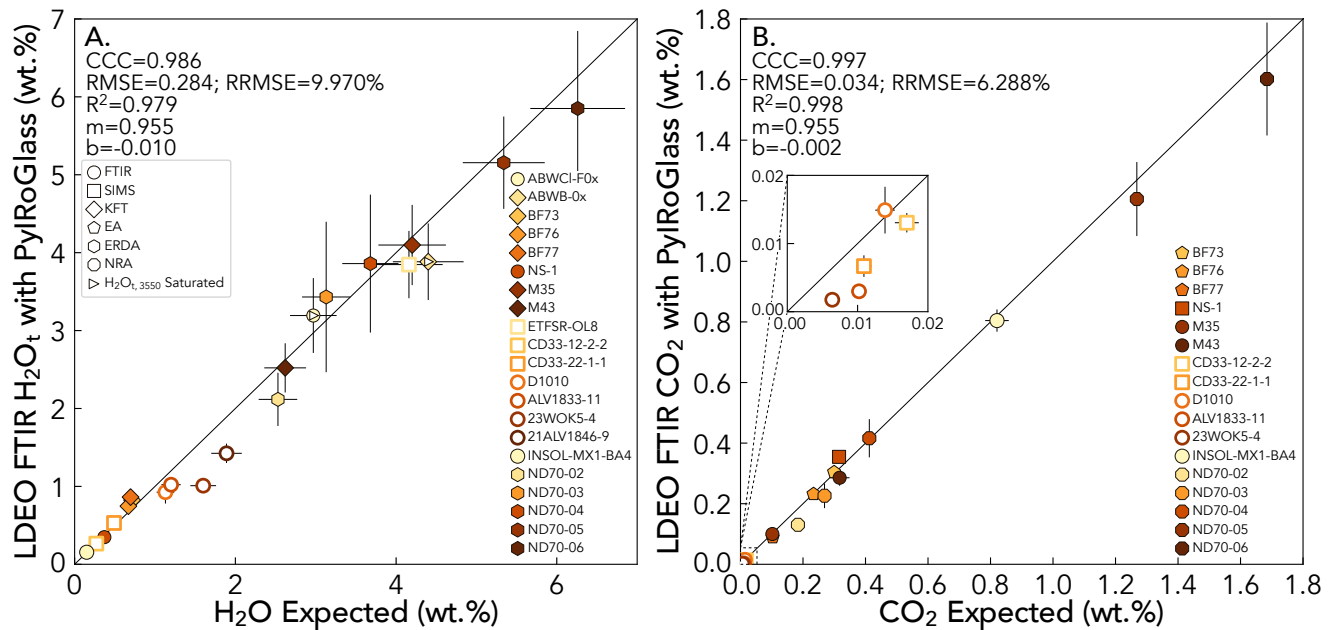


Figure 13: Comparison of volatile concentrations from PyIRoGlass and concentrations from published analyses by FTIR, SIMS, KFT, EA, ERDA, or NRA. 1  $\sigma$  uncertainties from PyIRoGlass propagate analytical, fitting, and replicate analysis uncertainties. A. H<sub>2</sub>O concentrations from FTIR vs. concentrations from FTIR, SIMS, KFT, or ERDA. Saturated samples H<sub>2</sub>O concentrations are represented by combining H<sub>2</sub>O<sub>m,1635</sub> and OH<sub>4500</sub><sup>-</sup>. Agreement within H<sub>2</sub>O concentrations is demonstrated by the high CCC, low RMSE (wt.% unit), low RRMSE of ~10% (unitless), high R<sup>2</sup>, *m* nearing 1, and *b* nearing 0. B. CO<sub>2</sub> concentrations by FTIR vs. concentrations from FTIR, SIMS, EA, or NRA. We use the molar absorptivities provided in each respective study to calculate CO<sub>2</sub> concentrations, for samples with published concentrations from FTIR (presented in Table 4). Agreement within CO<sub>2</sub> concentrations is demonstrated by the high CCC, low RMSE (wt.% unit), low RRMSE of ~6% (unitless), high R<sup>2</sup>, *m* nearing 1, and *b* nearing 0.

coefficients of determination (greater than 0.9) and low relative root-mean-square errors (less than 20%). The strength of the fit can be attributed to the lower noise within this region and the increased constraints associated with the volatiles below detection baselines. At 50  $\mu\text{m}$ , the detection limit for H<sub>2</sub>O<sub>m,1635</sub> is predicted to be 0.02 wt.% and for CO<sub>3</sub><sup>2-</sup> is predicted to be 47 ppm; at 100  $\mu\text{m}$ , these respectively decrease to 0.01 wt.% and 22 ppm.

The detection limits for the H<sub>2</sub>O<sub>m,5200</sub>, OH<sub>4500</sub><sup>-</sup>, and H<sub>2</sub>O<sub>t,3550</sub> peaks, with PyIRoGlass ALS sampled baselines, are associated with significantly more noise within the reciprocal function (Figure 14D, Figure 14E, Figure 14F). The reciprocal functions fitting these peaks have low coefficients of determination (between 0.1 and 0.2) and higher relative root-mean-square errors (greater than 75%). The weaker nature of this fit can be attributed to increased noise in the spectral region. The lower amplitude near-infrared H<sub>2</sub>O<sub>m,5200</sub> and OH<sub>4500</sub><sup>-</sup> peaks are associated with increased variability and noise; this translates to the detection limits associated with these peaks. The detection limits for H<sub>2</sub>O<sub>m,5200</sub> are approximately three times those for the H<sub>2</sub>O<sub>m,1635</sub> peak. This observation further lends credence to the observation of the higher quality of the H<sub>2</sub>O<sub>m,1635</sub> peak over the H<sub>2</sub>O<sub>m,5200</sub> peak (see Section 3.4). The detection limits for the mid-infrared H<sub>2</sub>O<sub>t,3550</sub> peak are low, but are similarly associated with variability and noise. At 50  $\mu\text{m}$ , the detection limit for H<sub>2</sub>O<sub>m,5200</sub> is predicted to be 0.06 wt.%, for OH<sub>4500</sub><sup>-</sup> is predicted to be 0.05 wt.%, and for

H<sub>2</sub>O<sub>t,3550</sub> is predicted to be 0.008 wt.%; at 100  $\mu\text{m}$ , these will respectively decrease to 0.05 wt.%, 0.03 wt.%, and 0.005 wt.%.

We thus quantify the detection limit, or minimum detectable signal, across a range of sample thicknesses extending to ~250  $\mu\text{m}$ . The entire uncertainty associated with FTIR may however be more significant based on the quality of the analyzed spectrum, which is influenced by spectral scans, spectral resolution, and aperture size. The spectra utilized to quantify detection limits were all acquired at 256 collection scans at 4 cm<sup>-1</sup> spectral resolution with the Thermo Scientific Nicolet iN10 MX FTIR Spectrometer with a liquid nitrogen-cooled MCT-A detector. Aperture sizes were maximized for each sample, with areas ranging from 150-10<sup>4</sup>  $\mu\text{m}^2$ . Spectra of lower quality or with more significant noise likely will see different detection limits. Future work may seek to further quantify the impacts of spectrum quality or aperture size on detection limits.

### 3.7 Chemistry Modulating the Baseline

Here, we explore the relationships between glass chemistry and the baseline in our validation and test datasets. Correlation coefficients between chemical components and the best-fit baseline-generating coefficients from PyIRoGlass are low, but these weak correlations may still provide some information. The coefficients impacting the baseline most significantly modify melt polymerization and structure—including



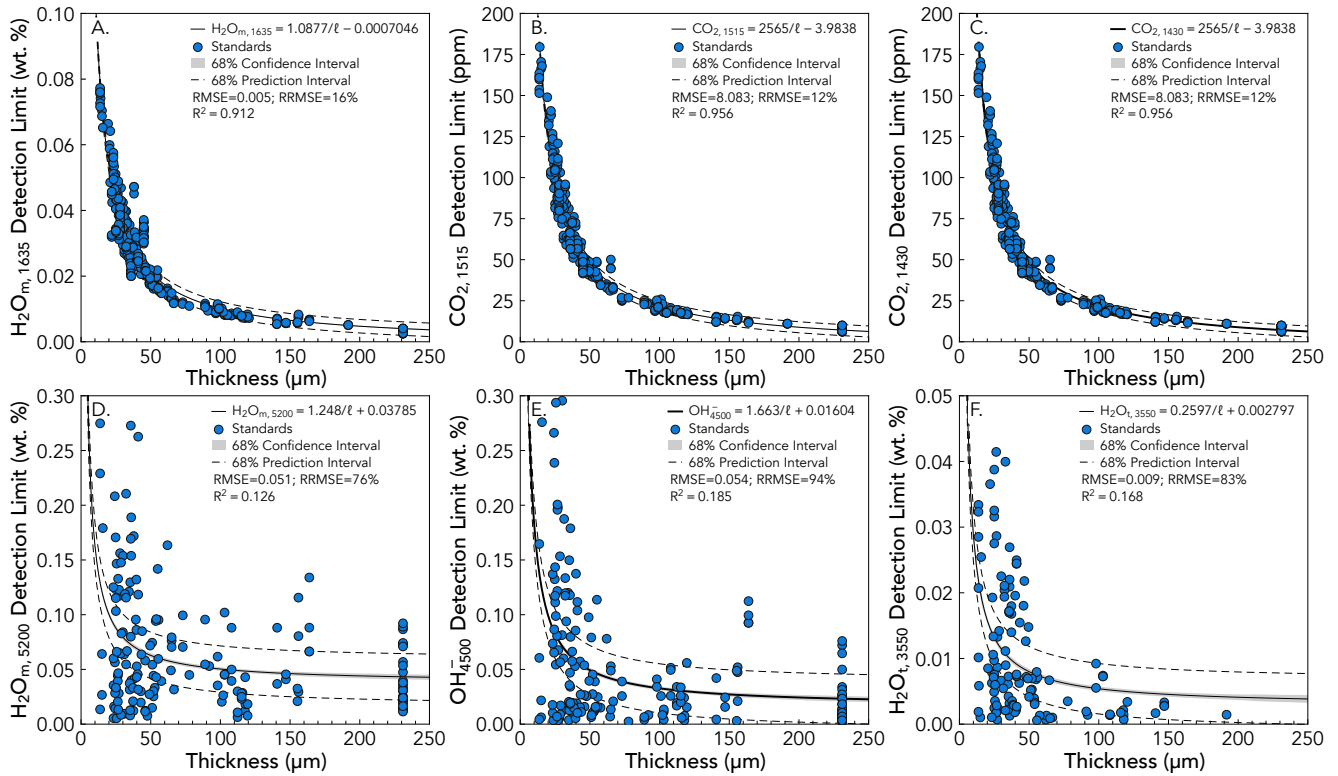


Figure 14: Detection limits across sample thickness for H<sub>2</sub>O and CO<sub>2</sub> volatile species in basaltic to andesitic glasses. Three times the standard deviation of the background signal is quantified from the PylRoGlass sampled baselines, and converted from the signal to concentration domain with the Beer-Lambert Law. The detection limit relationship with thickness takes the form of the reciprocal function, given the presence of thickness in the denominator of the Beer-Lambert Law. Three of the detection limit relationships with thickness are based upon baselines determined from the 10<sup>6</sup> PylRoGlass MCMC sampled baselines: A. H<sub>2</sub>O<sub>m,1635</sub>. B. CO<sub>2,1515</sub><sup>-</sup>. C. CO<sub>2,1430</sub><sup>-</sup>. These detection limits are well fit by the reciprocal function (R<sup>2</sup> greater than 0.9 and RRMSE less than 20%), given low noise in this mid-IR region with strong constraints upon the baseline. The other three detection limit relationships with thickness are based upon baselines determined from the ALS sampled baselines: D. H<sub>2</sub>O<sub>m,5200</sub>. E. OH<sub>4500</sub><sup>-</sup>. F. H<sub>2</sub>O<sub>t,3550</sub>. These detection limits are fit by the reciprocal function (R<sup>2</sup> between 0.1 and 0.2 and RRMSE greater than 75%), given more significant noise in the higher wavenumber region and lower amplitude near-IR H<sub>2</sub>O<sub>m,5200</sub> and OH<sub>4500</sub><sup>-</sup> peaks.

the network-forming tetrahedrally coordinated cations in SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and minor components Fe<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub>; the network-modifying alkali earth cations in CaO and MgO; silicate network-depolymerizing H<sub>2</sub>O (Figure 15). Notably, the commonly used parameter of non-bridging oxygens to tetrahedral cations (NBO/T) does not strongly correlate with any baseline-generating coefficient, while the individual network-forming, network-modifying, and network-depolymerizing components do [Mysen and Richet 2018; Mysen 2022].

Increasing the proportion of network-forming cations in SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>, sitting near the center of oxygen tetrahedra, appears to increase  $x_0$  or the best-fit coefficient altering the amplitude of the Baseline. The curvature of the baseline captured by  $x_1$ , which scales  $\text{Baseline}_{PC1}$ , can be described by the depolymerization of the melt and the decrease of NBO/T due to the increase of minor network-forming cations Fe<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> and depolymerizer H<sub>2</sub>O. Variations in oxidation state alter the extent of polymerization, with the oxidation of Fe<sup>2+</sup> to Fe<sup>3+</sup> increasing the NBO/T of the melt [Dingwell and Virgo 1987; Mysen 2022]. This relationship between oxidation state, extent of polymerization, and the baseline potentially

demonstrates some unintentional consequences for utilizing devolatilized baselines for fitting natural samples, since the experimental process of devolatilizing glasses can alter their oxidation state.  $x_2$  does not offer clear insights into the characteristics of the melt.  $x_3$ , scaling  $\text{Baseline}_{PC3}$ , demonstrates the same trends as  $x_1$ , but with stronger correlation coefficients for H<sub>2</sub>O and density.  $x_4$ , scaling  $\text{Baseline}_{PC4}$ , demonstrates the same trends as  $x_1$  and  $x_3$ , but with the additional impact of network-modifying cations. Decreasing the proportion of network-modifying cations MgO and CaO, which charge balance tetrahedrally coordinated Al<sup>3+</sup>, increases the amplitude of  $x_4$  [Mysen and Virgo 1986; Mysen 2022].

While the chemical variability of the glasses in the validation and test dataset provide some insight into the nature of the baseline, the baseline cannot be explicitly generated or empirically fit from solely glass chemistry. The necessity of the ensemble solution offered by PylRoGlass is underscored by the lack of a straightforward correlation between the baseline and chemistry within these datasets. A full understanding of these relationships remains elusive and is beyond the scope of this paper. The publication and availability of more glass



1305 spectra, with a wide range of chemical compositions, will allow for further exploration.

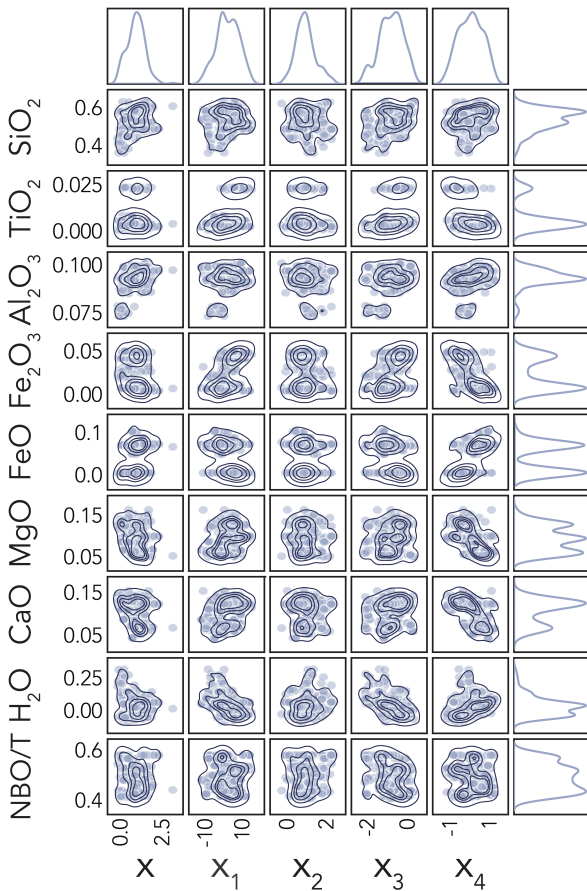


Figure 15: Posterior probability distributions of the baseline-generating coefficients, including  $x_0$  scaling  $\overline{\text{Baseline}}$  and  $x_{1-4}$  scaling  $\overline{\text{Baseline}}_{\text{PC}_{1-4}}$ , and chemical composition of the melt in the validation and test datasets.  $x_0$  is weakly correlated with  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$ .  $x_1$  is correlated with  $\text{Fe}_2\text{O}_3$ ,  $\text{FeO}$ ,  $\text{TiO}_2$ , and  $\text{H}_2\text{O}$ .  $x_2$  is uncorrelated.  $x_3$  is correlated with  $\text{Fe}_2\text{O}_3$ ,  $\text{FeO}$ , and  $\text{H}_2\text{O}$ .  $x_4$  is correlated with  $\text{Fe}_2\text{O}_3$ ,  $\text{FeO}$ ,  $\text{MgO}$ ,  $\text{CaO}$ , and  $\text{H}_2\text{O}$ .

## 4 CONCLUSIONS

1310 PyIRoGlass is a novel Bayesian method with MCMC sampling developed and validated for the purpose of reproducibly processing the transmission FTIR spectra of basaltic to andesitic glasses, where carbon is primarily dissolved as  $\text{CO}_3^{2-}$ , in the open-source Python language. The utility of PyIRoGlass emerges when devolatilized baselines are not readily available, which is particularly true of melt inclusion studies. All parameters within the Beer-Lambert Law—including the baseline, molar absorptivity, thickness, and density—are closely examined to quantify their associated uncertainties. Inverting for molar absorptivity as a function of compositional parameter properly quantifies both the uncertainty of the inversion and of the composition. PyIRoGlass allows for the sampling of all likely baselines and peaks to iteratively solve for the best-fit coefficients and parameters, in order to determine volatile concentrations with robust estimates of uncertainties.

PyIRoGlass is currently tuned to arc basalts and andesites; future work could identify the shapes and variability in the baselines for other compositions such as alkali basalts, dacites, and rhyolites. The performance of PyIRoGlass is dependent on the model and calibration inputs, with the input dataset of transmission FTIR spectra with volatiles below detection fundamentally determining the shape and variability of the baseline. As the dataset of spectra with volatiles below detection expands, our understanding of the shape and variability of the baseline might shift to fit a wider array of compositions. Composition-dependent calibrations of molar absorptivity might similarly change as datasets evolve. Open-sourcing this Python code encourages iterative development and enhancement. Future validation may target further analysis of the relationships between composition and baseline variability for improved sampling of parameter space, as well as between composition and molar absorptivity. Further development of PyIRoGlass will focus on the expansion of this open-source package for processing rhyolitic glasses, where carbon is primarily dissolved as  $\text{CO}_2$ .

## AUTHOR CONTRIBUTIONS

SCS, WHT, TP, and AB conceived the project. SCS wrote the manuscript, collected the Volcán de Fuego melt inclusion validation dataset and some of the test dataset, developed most of the Python code, documented the code, and interpreted the results. WHT performed the principle component analysis for fitting the  $\text{CO}_3^{2-}$  doublet and  $\text{H}_2\text{O}_{\text{m},1635}$  peak and wrote the initial MCMC parameter fitting code. TP helped scope the devolatilized baseline approach, provided guidance and support, and edited the manuscript. AB helped with data collection and interpretation, and tested the code. DR analyzed the dataset of melt inclusions with volatiles below detection. YM and HL synthesized, analyzed, and provided glasses for validation and testing. WM developed the inversion code with SCS for determining molar absorptivities and critically contributed to understandings of robust uncertainty and error analysis. All authors provided feedback on the results and manuscript.

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## DATA AVAILABILITY

All data and code are available on GitHub (github.com/sarahshi/PylRoGlass), with documentation and examples at Read The Docs (pyrirogl. readthedocs.io). The code (Version 0.6.1) and data from this manuscript are archived on Zenodo (DOI:10.5281/zenodo.10883628). The code can be run through the Google Colab cloud server (colab.research.google.com/github/SarahShi/PylRoGlass/blob/main/PylRoGlass\_RUN\_colab.ipynb). The supplement contains information on the code package structure, datasets, inversion techniques, and analytical methodologies.

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